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(54) **Method for producing palladium complex compound**

Verfahren zur Herstellung einer Palladiumkomplexverbindung

Procédé de préparation d'un complexe de palladium

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(73) Proprietor: **Central Glass Company, Limited**
Ube-shi, Yamaguchi 755-0001 (JP)

(72) Inventors:
- **Kume, Takashi, c/o Chemical Research Center of Kawagoe-shi, Saitama 350-1151 (JP)**
- **Narizuka, Satoru, c/o Chemical Research Center of Kawagoe-shi, Saitama 350-1151 (JP)**
- **Koide, Makoto, c/o Chemical Research Center of Kawagoe-shi, Saitama 350-1151 (JP)**
- **Mikami, Koichi Yokohama-shi, Kanagawa 231-0037 (JP)**
- **Hatano, Manabu Tokyo 140-0011 (JP)**
- **Terada, Masahiro Urawa-shi, Saitama 336-0022 (JP)**
- **Ishida, Michio, c/o Chemical Research Center of Kawagoe-shi, Saitama 350-1151 (JP)**
- **Morino, Yuzuru, c/o Chemical Research Center of Ube-shi, Yamaguchi 755-0001 (JP)**

(74) Representative:
Manitz, Finsterwald & Partner GbR
Postfach 31 02 20
80102 München (DE)

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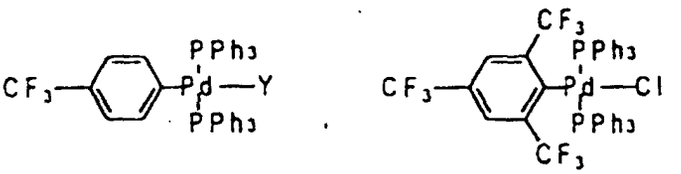
Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a method for producing a palladium-phosphine complex compound, which is useful as a catalyst of organic synthesis.

[0002] Hitherto, various transition metal complexes have been used as catalysts of organic synthesis. In particular, noble metal complexes are stable and easy to handle. Thus, they are widely used as catalysts for organic synthesis, although they are high in price. Of optically active ligands of transition metal complexes used in asymmetric catalytic reactions, a ligand of 2,2'-bis(diphenylphosphino)-1,1'-binaphtyl (hereinafter referred to as "BINAP") is one of the most superior ligands in asymmetry differentiation capability. It has been reported in J. Am. Chem. Soc., 1991, Vol. 113, pp. 1417 and J. Org. Chem., 1989, Vol. 54, pp. 4738 that a palladium complex having a ligand of BINAP is very much superior in catalytic activity, particularly in enantio-selectivity, for Heck reaction to an olefin, which is an asymmetric carbon-carbon bond formation reaction. In such reaction, there is assumed an involvement of an intermediate of [PhPd (I)(BINAP)], which is formed by an oxidative addition of benzene iodide to Pd(O)-BINAP formed in the reaction system.

[0003] There are known palladium complex compounds having ligands of trifluoromethylphenyl and tris(trifluoromethyl)phenyl, which are represented by the general formulas:



where Y is fluorine, chlorine, bromine, or iodine.

[0004] J. Organomet. Chem., 1971, 28, 287 discloses a method for producing a palladium complex compound represented by the general formula $Ar^1Pd(PPh_3)_2X^1$ where Ar^1 represents an aryl and X^1 is a halogen. In this method, a stable palladium complex $Pd^0(PPh_3)_4$ is reacted with an aryl halide. J. Organometallics, 1996, 15(17), 3708 discloses a similar method in which a palladium complex $Pd_2(dba)_3$ is used.

[0005] J. Chem. Commun., 1994, 121 discloses a reaction of dibromobis(triphenylphosphine)palladium(II) with toluene in the presence of potassium carbonate at 130°C for 1 hr to obtain a small amount of bromo[methylphenyl]bis (triphenylphosphine)palladium(II).

[0006] J. Am. Chem. Soc., Vol. 117, No. 15, 4305 (1995) discloses a method for producing a palladium complex compound having a benzoato ligand, represented by the formula $(Ph_3P)_2PdPh(PhCOO)$. In this method, $(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2$ is dispersed in benzene. Then, benzoic acid is added to the mixture to have a solution having a pale yellow color. Then, the solvent is distilled away. After that, n-hexane is added, thereby obtaining $(Ph_3P)_2Pd_2Ph_2(\mu\text{-}PhCOO)_2$ in the form of crystal. The obtained crystals are dispersed in benzene. Then, triphenylphosphine is added, thereby preparing a transparent solution. Then, the solvent is distilled away. After that, n-hexane is added, thereby obtaining the aimed palladium complex compound in the form of crystal.

[0007] J. Oraganomet. Chem. 553 (1998) 83-90 discloses a method for producing trans-[Pd(OOC-(C_6H_4)-2-SMe-κ^1-O)Ph(PPh_3)$_2$]. In this method, a thallium salt 2-RS-C_6H_4-COOTl is prepared by reacting 2-RS-C_6H_4-COOH with thallium carbonate in ethanol. Then, the thallium salt is reacted with trans-[PdCl(Ph)(PPh_3)$_2$] in tetrahydrofuran, thereby obtaining the product with a precipitate of thallium chloride.

SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to provide a method for easily producing a palladium complex compound that is useful as catalyst.

[0009] It is another object of the present invention to provide a palladium complex compound that is superior in physical and/or chemical properties.

[0010] According to a first aspect of the present invention, there is provided a first method for producing a first palladium-complex compound represented by the general formula (4). With this, it is possible to easily obtain the product by the following reaction steps (a) and (b). The first method comprises:

(a) reacting an aromatic compound represented by the general formula (1), with a palladium compound and a phosphine derivative, in the presence of a first basic substance, thereby obtaining a second palladium-complex

compound represented by the general formula (2); and
(b) reacting said second palladium-complex compound with a benzoic acid represented by the general formula (3), in the presence of a second basic substance, thereby producing said first palladium-complex compound,

$$Ar^1X \quad (1)$$

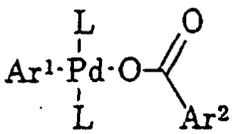
where Ar^1 is an aryl group; and X is a halogen that is fluorine, chlorine, bromine or iodine, trifluoromethanesulfonate group, an alkylsulfonate group having a carbon atom number of 1-4, or a substituted or unsubstituted arylsulfonate group,

$$Ar^1\text{-}PdL_2X \quad (2)$$

where each L is independently a phosphine ligand, and Ar^1 and X are defined as above,

$$Ar^2\text{-}COOH \quad (3)$$

where Ar^2 is an aryl group,

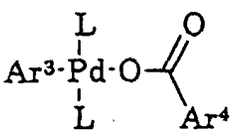


(4)

where Ar^1, Ar^2, and L are defined as above.

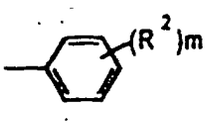
[0011] According to a second aspect of the invention, there is provided a second method for producing the first palladium-complex compound represented by the general formula (4). As compared with the first method, the second method comprises a single reaction step of reacting an aromatic compound represented by the general formula (1), with a palladium compound, a phosphine derivative and a benzoic acid derivative represented by the general formula (3), in the presence of a basic substance, thereby obtaining the first palladium-complex compound.

[0012] According to a third aspect of the invention, there is provided a novel palladium complex compound. This compound, which can be produced by the above-mentioned first, or second method, is represented by the general formula (5),



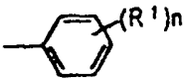
(5)

where Ar^3 and Ar^4 are respectively aryl groups represented by the general formulas (6) and (7), and each L is independently a phosphine ligand,



(6)

where R^2 is trifluoromethyl group, trifluoromethyloxy group, a halogen that is fluorine, chlorine, bromine or iodine, nitro group, acetyl group, cyano group, an alkyl group having a carbon atom number of 1-4, an alkoxyl group having a carbon atom number of 1-4, or an alkoxycarbonyl group having a carbon atom number of 2-5; and m is an integer of 0-4,



(7)

where R^1 is trifluoromethyl group, and n is an integer of 1-3.

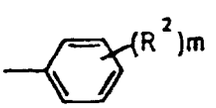
[0013] The following palladium complex compound, which can be produced by step (a) of the above-mentioned first method, is represented by the general formula Ar^5-PdL_2X where Ar^5 is bis(trifluoromethyl)phenyl group, X is a halogen that is fluorine, chlorine, bromine or iodine, and each L is independently a phosphine ligand.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] The above-mentioned first and second methods according to the invention will be described in detail, as follows.

[0015] In the aromatic compound Ar^1X used in the first and second methods X is defined as above and preferably bromine or iodine in practical use.

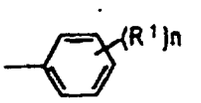
[0016] In the aromatic compound Ar^1X used in the first and second methods. Ar^1 is defined as being an aryl group, as mentioned above. This aryl group Ar^1 can be selected from carbon cyclic groups, such as phenyl and naphthyl, and heterocyclic groups, such as pyridyl and quinolyl. These groups may have substituents. The aryl group Ar^1 is preferably one represented by the general formula (6),



(6)

where R^2 is a halogen that is fluorine, chlorine, bromine or iodine, or a monovalent organic group, and m is an integer of 0-4. The substituent R^2 is not particularly limited so long as it is inert in the reaction of the invention.

[0017] In the benzoic acid Ar^2-COOH used in the first and second methods, Ar^2 is also defined as being an aryl group, as mentioned above. This aryl group Ar^2 can also be selected from the above-mentioned exemplary groups of the aryl group Ar^1. The exemplary groups of the aryl group Ar^2 may also have substituents. The aryl group Ar^2 is preferably one represented by the general formula (7),



(7)

where R^1 is defined as R^2 of the general formula (6) and n is an integer of 0-3. The substituent R^1 is not particularly limited so long as it is inert in the reaction of the invention.

[0018] Examples of the substituents R^1 and R^2 in the general formulas (6) and (7) are trifluoromethyl group, trifluoromethyloxy group, halogens that are fluorine, chlorine, bromine and iodine, nitro group, acetyl group, cyano group, alkyl groups each having a carbon atom number of 1-4, alkoxyl groups each having a carbon atom number of 1-4, and alkoxycarbonyl groups each having a carbon atom number of 2-5. Examples of the alkyl group are methyl group, ethyl group, n-propyl group, and i-propyl group. Examples of the alkoxyl group are methoxy group, ethoxy group, n-propoxy group, and i-propoxy group. Examples of the alkoxycarbonyl group are methoxycarbonyl group, ethoxycarbonyl group, n-propoxycarbonyl group, and i-propoxycarbonyl group. The aryls group Ar^1 is preferably one in which at least one of R^2 is trifluoromethyl group. The aryl group Ar^2 is also preferably one in which at least one of R^1 is trifluoromethyl group.

[0019] Examples of the aryl groups Ar^1 and Ar^2 used in the first and second methods are (1) aryl groups each having one trifluoromethyl, such as 2-trifluoromethylphenyl, 3-trifluoromethylphenyl, and 4-trifluoromethylphenyl, (2) aryl groups each having one trifluoromethoxy, such as 2-trifluoromethoxyphenyl, 3-trifluoromethoxyphenyl, and 4-trifluoromethoxyphenyl, (3) aryl groups each having one fluorine, such as 2-fluorophenyl, 3-fluorophenyl, and 4-fluorophenyl, (4) aryl groups each having one chlorine, such as 2-chlorophenyl, 3-chlorophenyl, and 4-chlorophenyl, (5) aryl groups each having one bromine, such as 2-bromorophenyl, 3-bromorophenyl, and 4-bromorophenyl, (6) aryl groups each having one iodine, such as 2-iodophenyl, 3-iodophenyl, and 4-iodophenyl, (7) aryl groups each having one nitro group, such as 2-nitrophenyl, 3-nitrophenyl, and 4-nitrophenyl, (8) aryl groups each having one acetyl, such as 2-acetylphenyl, 3-acetylphenyl, and 4-acetylphenyl, (9) aryl groups each having one cyano group, such as 2-cyanophenyl, 3-cyano-

phenyl, and 4-cyanophenyl, (11) aryl groups each having one alkyl, such as 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 3-ethylphenyl, and 4-ethylphenyl, (12) aryl groups each having one alkoxy, such as 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-ethoxyphenyl, 3-ethoxyphenyl, and 4-ethoxyphenyl, and (13) aryl groups each having one alkoxycarbonyl, such as 2-methoxycarbonylphenyl, 3-methoxycarbonylphenyl, 4-methoxycarbonylphenyl, 2-ethoxycarbonylphenyl, 3-ethoxycarbonylphenyl, and 4-ethoxycarbonylphenyl. Each of the aryl groups Ar^1 and Ar^2 may have at least two substituents. These at least two substituents may be any arbitrary combination of various substituents. One of the at least two substituents of the aryl group Ar^1 or Ar^2 is preferably trifluoromethyl group. Nonlimitative examples of such aryl groups Ar^1 and Ar^2 are

2-chloro-3-(trifluoromethyl)phenyl,
2-fluoro-3-(trifluoromethyl)phenyl,
2-fluoro-4-(trifluoromethyl)phenyl,
3-fluoro-5-(trifluoromethyl)phenyl,
2-bromo-6-(trifluoromethyl)phenyl,
4-chloro-2-(trifluoromethyl)phenyl,
4-fluoro-2-(trifluoromethyl)phenyl,
2-chloro-6-(trifluoromethyl)phenyl,
4-fluoro-3-(trifluoromethyl)phenyl,
1-chloro-4-(trifluoromethyl)phenyl,
2-fluoro-6-(trifluoromethyl)phenyl,
2-fluoro-5-(trifluoromethyl)phenyl,
2-chloro-4-(trifluoromethyl)phenyl,
4-chloro-3-(trifluoromethyl)phenyl,
4-chloro-2-(trifluoromethyl)phenyl and the like;
2-methyl-3-(trifluoromethyl)phenyl,
3-methyl-5-(trifluoromethyl)phenyl,
2-methyl-4-(trifluoromethyl)phenyl,
4,5-dimethyl-2-(trifluoromethyl)phenyl,
2-methyl-5-(trifluoromethyl)phenyl,
5,6-dimethyl-2-(trifluoromethyl)phenyl,
4ethyl-3-(trifluoromethyl)phenyl, and the like;
2-methoxy-4-(trifluoromethyl)phenyl,
2-ethoxy-4-(trifluoromethyl)phenyl,
4-ethoxy-2-(trifluoromethyl)phenyl,
4-methoxy-2-(trifluoromethyl)phenyl,
2-methoxy-5-(trifluoromethyl)phenyl, and the like;
2-nitro-3-(trifluoromethyl)phenyl,
2-nitro-4-(trifluoromethyl)phenyl,
4-nitro-2-(trifluoromethyl)phenyl,
3-nitro-5-(trifluoromethyl)phenyl,
2-nitro-5-(trifluoromethyl)phenyl,
4-nitro-3-(trifluoromethyl)phenyl, and the like;
2-cyano-5-(trifluoromethyl)phenyl,
2-cyano-4-(trifluoromethyl)phenyl,
4-fluoro-3-cyano-5-(trifluoromethyl)phenyl,
4-cyano-3-(trifluoromethyl)phenyl,
2-chloro-5-cyano-3-(trifluoromethyl)phenyl,
4-cyano-2-(trifluoromethyl)phenyl, and the like; and
2-amino-6-(trifluoromethyl)phenyl,
2-amino-5-(trifluoromethyl)phenyl,
2-amino-4-(trifluoromethyl)phenyl,
2-amino-3-(trifluoromethyl)phenyl,
3-amino-6-(trifluoromethyl)phenyl,
3-amino-5-(trifluoromethyl)phenyl,
4-amino-2-(trifluoromethyl)phenyl,
4-amino-3-(trifluoromethyl)phenyl, and the like. Each aryl group Ar^1 or Ar^2 is preferably one having at least two trifluoromethyl groups. Examples of such aryl group are

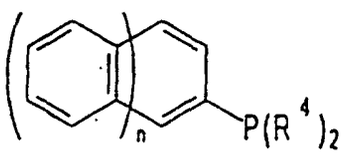
2,3-bis(trifluoromethyl)phenyl, 2,4-bis(trifluoromethyl)phenyl,
2,5-bis(trifluoromethyl)phenyl, 2,6-bis(trifluoromethyl)phenyl,

3,4-bis(trifluoromethyl)phenyl, and
3,5-bis(trifluoromethyl)phenyl. Further nonlimitative examples of such aryl group are
2,3,4-tris(trifluoromethyl)phenyl,
2,4,5-tris(trifluoromethyl)phenyl,
2,3,5-tris(trifluoromethyl)phenyl,
1,3,5-tris(trifluoromethyl)phenyl,
3,4,5-tris(trifluoromethyl)phenyl,
2,3,4,6-tetrakis(trifluoromethyl)phenyl,
1-bromo-2,3,4-tris(trifluoromethyl)phenyl,
2-bromo-4,5,6-tris(trifluoromethyl)phenyl, and the like; and
3,5-dichloro-4,6-bis(trifluoromethyl)phenyl,
2-dichloro-3,5-bis(trifluoromethyl)phenyl,
2-methoxy-3,5-bis(trifluoromethyl)phenyl,
2-bromo-3,5-bis(trifluoromethyl)phenyl,
2-nitro-4,6-bis(trifluoromethyl)phenyl,
5,6-dichloro-1,3-bis(trifluoromethyl)phenyl,
4-chloro-3,5-bis(trifluoromethyl)phenyl, and the like.

[0020] The second palladium-complex compound (Ar^1-PdL_2X), prepared in step (a) of the first method of the invention, is preferably one in which at least one of R^2 is trifluoromethyl group and more preferably one in which at least two of R^2 are trifluoromethyl groups, since the aimed product becomes extremely useful. The benzoic acid (Ar^2-COOH), which is used in the first and second methods of the invention, is preferably one in which at least one of R^1 is trifluoromethyl group and more preferably one in which at least two of R^1 are trifluoromethyl groups, since the aimed product becomes extremely useful.

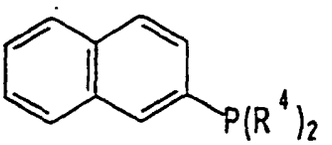
[0021] As stated above, the second palladium-complex compound represented by the general formula (2), Ar^1-PdL_2X, where each L is independently a phosphine ligand, is prepared in step (a) of the first method. Furthermore, the phosphine derivative is used in the first and second methods. Such phosphine (phosphine derivative or phosphine ligand) used in the first and second methods is not particularly limited and may be one represented by the general formula $P(R^1)_3$, which can be a monodentate ligand in Ar^1-PdL_2X, where each R^1 is independently a first group selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group. The first group optionally has a first substituent R^2 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a second substituent. The second substituent is selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group. The second substituent optionally has a third substituent R^3 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a substituent being selected from the group consisting of lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group. The substituent optionally has a substituent. In the present application, "lower alkyl groups", for example, of the above-mentioned phosphine, can be straight chain or branched alkyl groups each having a carbon atom number of 1-6. Examples of such lower alkyl groups are methyl group (hereinafter may be referred to as "Me"), ethyl group, n-propyl group, i-propyl group, n-butyl group, sec-butyl group, tert-butyl group, n-pentyl group, and n-hexyl group. In the present application, "lower alkoxy groups", for example, of the above-mentioned phosphine can be straight chain or branched alkoxy groups each having a carbon atom number of 1-6. Examples of such lower alkoxy groups are methoxy group (hereinafter may be referred to as "MeO"), ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, sec-butoxy group, tert-butoxy group, n-pentoxy group, and n-hexyloxy group.

[0022] In the above-mentioned phosphine represented by the general formula $P(R^1)_3$, at least one of R^1 is preferably phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-acynyl group, or 3,5-xylyl group. Concrete examples of such phosphine are triphenylphosphine, tris(o-tolyl)phosphine, tris(m-tolyl)phosphine, tris(p-tolyl)phosphine, tris(4-acynyl) phosphine, tris(3,5-xylyl)phosphine, and tris(n-butyl)phosphine. Of these, triphenylphosphine is particularly preferable. The phosphine $P(R^1)_3$ can be a first one represented by the following formula:

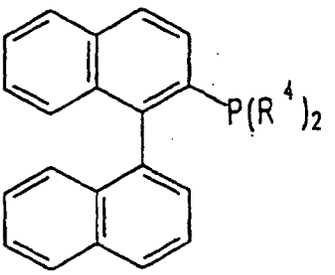


where n is an integer of 1-2, an arbitrary number of hydrogen atoms of the condensed ring may be replaced with the

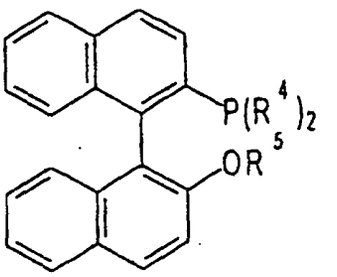
above-defined first substituent R^2, and each R^4 is independently phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-acynyl group, or 3,5-xylyl group. Such phosphine $P(R^1)_3$ can be a second one represented by the following formula:



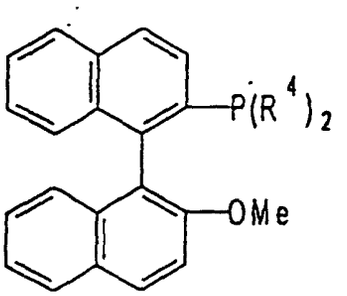
where an arbitrary number of hydrogen atoms of the naphthalene ring may be replaced with the above-defined first substituent R^2, and each R^4 is defined as above. Furthermore, the phosphine $P(R^1)_3$ can be a third one represented by the following formula:



where an arbitrary number of hydrogen atoms of the naphthalene ring may be replaced with lower alkyl groups or lower alkoxy groups, and each R^4 is defined as above. Furthermore, the phosphine $P(R^1)_3$ can be a fourth one represented by the following formula

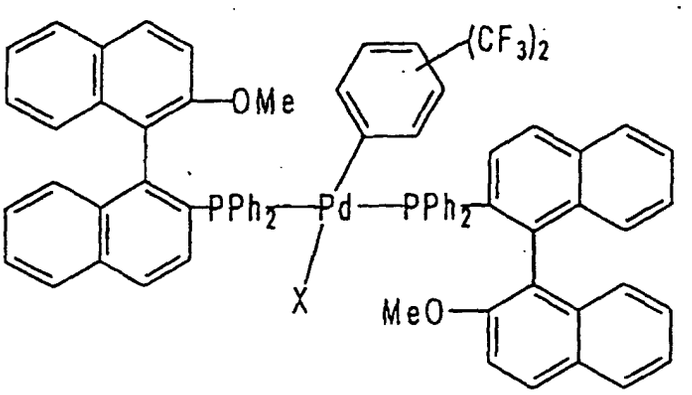


where R^5 is a lower alkyl group, and each R^4 is defined as above. Furthermore, the phosphine $P(R^1)_3$ can be fifth one represented by the following formula:



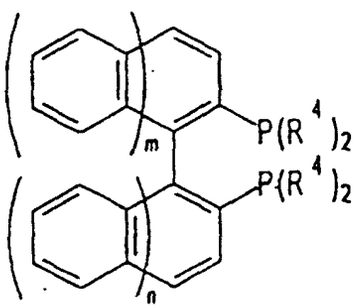
where each R^4 is defined as above. A preferable example of the second palladium-complex compound containing the above fifth phosphine, which can be used as the starting material of the third method, is one represented by the following

formula:

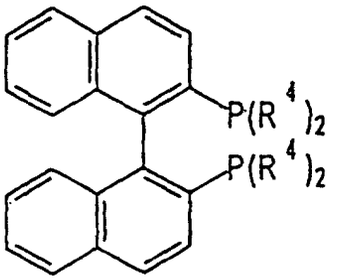


where X is a halogen that is fluorine, chlorine, bromine or iodine, trifluoromethanesulfonate group, an alkylsulfonate group having a carbon atom number of 1-4, or a substituted or unsubstituted arylsulfonate group. In this second palladium-complex compound, X is preferably bromine, and two of the trifluoromethyl group are particularly preferably bonded to the 3- and 5-positions.

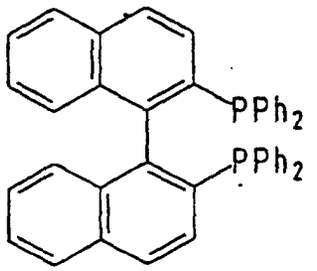
[0023] The phosphine (i.e., phosphine derivative or phosphine ligand) used in the first and second methods may be one represented by the general formula $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$, which can be a bidentate ligand in $Ar^1\text{-}PdL_2X$, where each R^1 is defined as in the phosphine $P(R^1)_3$, and Q is a bivalent group. In the phosphine $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$, at least one of R^1 is preferably phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-acynyl group, or 3,5-xylyl group. The bivalent group Q may comprise (1) an arbitrary number of a first bivalent group selected from alkylene group, phenylene group, naphthylene group, and anthrylene group, and (2) an arbitrary number of a bonding group selected from the group consisting of single bond, -O-, -S-, C(=O)-, and -S(=O)-. The first bivalent group optionally has an arbitrary number of a substituent that can be selected from nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group. The bivalent group Q can be a preferable one selected from alkylene group, biphenylene group, binaphthylene group and bianthrylene group. This preferable one optionally has an arbitrary number of a group selected from nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group. The phosphine $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$ can be a first one represented by the following general formula:



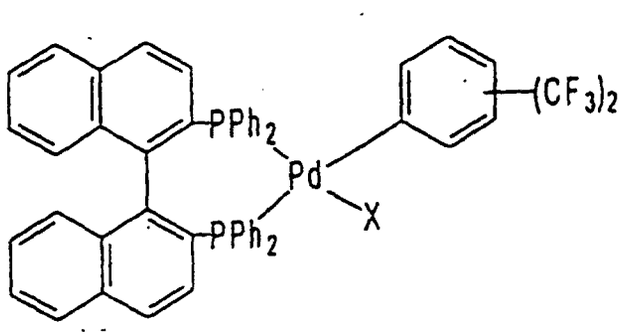
where an arbitrary number of hydrogen atoms of each aromatic ring may be replaced with the above-defined first substituent R^2, R^4 is defined as in the first one of the phosphine $P(R^1)_3$, each of m and n is independently an integer of 0-2. Furthermore, the phosphine $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$ can be a second one represented by the following general formula:



where an arbitrary number of hydrogen atoms of each aromatic ring may be replaced with the above-defined first substituent R^2, and R^4 is defined as in the first one of the phosphine $P(R^1)_3$. Furthermore, the phosphine $(R^1)_2P$-Q-P $(R^1)_2$ can be a third one represented by the following general formula:



where an arbitrary number of hydrogen atoms of each aromatic ring may be replaced with a lower alkyl group or a lower alkoxy group. A preferable example of the second palladium-complex compound containing the above third phosphine $(R^1)_2P{\cdot}Q{\cdot}P(R^1)_2$, which can be used as the starting material of the third method, is one represented by the following formula:



where X is a halogen that is fluorine, chlorine, bromine or iodine, trifluoromethanesulfonate group, an alkylsulfonate group having a carbon atom number of 1-4, or a substituted or unsubstituted arylsulfonate group. In this second palladium-complex compound, X is preferably bromine, and two of the trifluoromethyl group are particularly preferably bonded to the 3- and 5-positions.

[0024] The phosphine (i.e., the phosphine derivative or phosphine ligand) may be one represented by the general formula $(R^4)_2P$-$(CH_2)_q$-$P(R^4)_2$ where R^4 is defined as above, and q is an integer of 2-8. Furthermore, the phosphine may be one represented by the general formula Ph_2P-$(CH_2)_q$-PPh_2 where q is an integer of 2-8.

[0025] The palladium compound, which is used in the first and second methods, is preferably a palladium salt, such as palladium acetate, palladium chloride, palladium bromide, palladium iodide, or palladium nitrate. Furthermore, the palladium compound can be a palladium-complex(II), such as $[Pd(NH_3)_4]Y_2$, $Pd(NH_3)_2Y_2$, $Pd(NH_3)_4$, or PdY_4, where Y is halogen that is chlorine, bromine or iodine.

[0026] The basic substance, which is used in the first and second methods, including each of the first and second basic substances used in the first method, is not limited to a particular type. Nonlimitative examples of the basic sub-

stance are (i) ammonia and the like, such as ammonia and hydroxyamine, (2) amines, such as primary amine, secondary amine, tertiary amine, alicyclic amine (e.g., cyclopropylamine), and aromatic amine, and (a) inorganic bases, such as acetate (e.g., sodium acetate and potassium acetate), sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. Examples of the primary amine are propylamine, isopropylamine, butylamine, amylamine, and hexylamine. Examples of the secondary amine are diethylamine, dipropylamine, diisopropylamine, and dibutylamine. Examples of the third amine are triethylamine, tripropylamine, and tributylamine. Examples of the aromatic amine are triarylamine, N,N-dimethylaniline, N,N-diethylaniline, pyridine, and N-methylmorpholine.

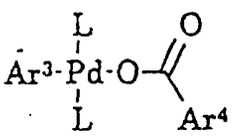
[0027] It is optional to use a solvent in the first and second methods of the invention. Examples of such solvent are (1) aliphatic hydrocarbons, such as pentane, hexane, heptane, and octane, (2) aromatic hydrocarbons, such as benzene, toluene, and xylene, (3) ethers, such as diethyl ether, dioxane, tetrahydrofuran (THF), and ethylene glycol dimethyl ether, (4) ketones, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, (5) nitriles such as acetonitrile, (6) tertiary amines such as pyridine, (7) acid amides, such as N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc), (8) sulfur-containing compounds, such as dimethylsulfoxide (DMSO) and sulforane, and (9) water. In case that a water-soluble basic substance is used in the reaction, it is preferable to use water, optionally together with one other solvent. Furthermore, the aromatic compound Ar^1X itself, which is used in the first and second methods, can be used as a reaction solvent.

[0028] According to the second method of the invention, it is essentially possible to complete the reaction in a single reaction vessel. Therefore, it becomes possible to remarkably simplify the reaction procedures. It is optional to modify the reaction of the second method by providing several reaction steps.

[0029] In the first and second methods of the invention, the respective amounts of the raw materials used in the reaction are not particularly limited. In fact, it is preferable to use at least one mole of the aromatic compound Ar^1X and at least two moles of the phosphine derivative, relative to 1 mol of palladium of the palladium compound, in the reaction step (a) of the first method. Furthermore, it is preferable to use at least one mole of the benzoic acid Ar^2-COOH, relative to one mol of palladium of the second palladium-complex compound Ar^1-PdL_2X, in the reaction step (b) of the first method. Similarly, it is preferable to use at least one mole of the aromatic compound Ar^1X, at least one mole of the benzoic acid Ar^2-COOH, and at least two moles of the phosphine derivative, relative to 1 mol of palladium of the palladium compound, in the second method. In the first and second methods, the respective amounts of the other raw materials, such as the basic substance and the solvent, are not particularly limited, and they can be used in respective suitable amounts.

[0030] The reaction in each of the first and second methods may be conducted as follows, and the following manner can be modified suitably. At first, a reaction vessel is charged with the raw materials (for example, in the case of the step (a) of the first method, the aromatic compound Ar^1X, the palladium compound, the phosphine derivative, the basic substance, and optionally solvent). The reaction vessel may or may not be pressurized and may or may not be stirred. The charged raw materials may or may not be heated to conduct the reaction, and the reaction may be conducted at a temperature of about 0-200°C, preferably of about 50-150°C to accelerate the reaction. After the reaction, the reaction vessel may be cooled down, and then the contents of the reaction vessel are taken out. Then, an extraction solvent may be added to the contents, thereby separating solid matter. After that, volatile substances are distilled off from the filtrate, thereby obtaining the aimed product (e.g., the second palladium-complex compound in the step (a) of the first method). If necessary, the aimed product can be purified through recrystallization, silica gel chromatography, or the like.

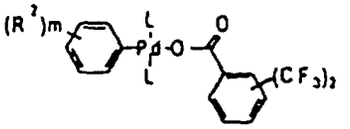
[0031] The above-stated novel first and second palladium complex compounds according to the third aspect of the invention will be described in detail, as follows. The first palladium complex compound, which can be produced by the first or second method, is represented by the general formula (5):



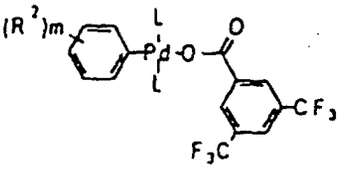
(5)

where Ar^3 and Ar^4 are respectively aryl groups represented by the above general formulas (6) and (7), and each L is independently a phosphine ligand. In the general formula (6) representing Ar^3, R^2 is trifluoromethyl group, trifluoromethyloxy group, a halogen that is fluorine, chlorine, bromine or iodine, nitro group, acetyl group, cyano group, an alkyl group having a carbon atom number of 1-4, an alkoxyl group having a carbon atom number of 1-4, or an alkoxycarbonyl group having a carbon atom number of 2-5. Examples of these alkyl group, alkoxy group and alkoxycarbonyl groups of Ar^3 are the same as the above-stated examples of those groups of Ar^1. In the general formula (7) representing Ar^4, R^1 is trifluoromethyl group. Examples of the aryl group Ar^4 are (1) aryl groups each having one trifluoromethyl, such as 2-trifluoromethylphenyl, 3-trifluoromethylphenyl, and 4-trifluoromethylphenyl, and (2) aryl groups each having

two trifluoromethyl groups, such as 2,3-bis(trifluoromethyl)phenyl, 2,4-bis(trifluoromethyl)phenyl, 2,5-bis(trifluoromethyl)phenyl, 2,6-bis(trifluoromethyl)phenyl, 3,4-bis(trifluoromethyl)phenyl, and 3,5-bis(trifluoromethyl)phenyl. Of these, an aryl group having two trifluoromethyl groups is preferable, and 3,5-bis(trifluoromethyl)phenyl is more preferable. Thus, the palladium complex compound represented by the general formula (5) is preferably one represented by the following general formula:

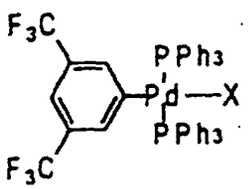


where R^2, m and L are defined as above. Furthermore, it is more preferably one represented by the following general formula:

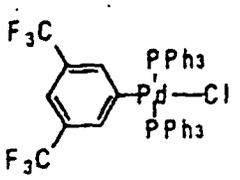


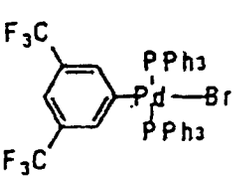
where R^2, m and L are defined as above. Similar to the aryl groups Ar^1 and Ar^2, the aryl group Ar^3 is preferably one in which at least one of R^2 is trifluoromethyl group. Examples of the aryl group Ar^3 are the same as those of the aryl groups Ar^1 and Ar^2. The aryl group Ar^3 may have at least two substituents. These at least two substituents may be any arbitrary combination of various substituents. One of the at least two substituents of the aryl group Ar^3 is preferably trifluoromethyl group. Nonlimitative examples of such aryl group Ar^3 are the same as those of the aryl groups Ar^1 and Ar^2. The aryl group Ar^3 is preferably one having at least two trifluoromethyl groups. Examples of such aryl group are the same as those of the aryl group Ar^1 or Ar^2. Further nonlimitative examples of the aryl group Ar^3 are the same as those of the aryl group Ar^1 or Ar^2.

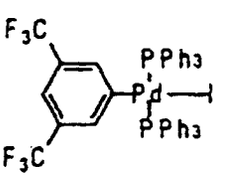
[0032] As stated above, the second palladium complex compound, which is produced by step (a) of the first method, is represented by the general formula Ar^5-PdL_2X where Ar^5 is bis(trifluoromethyl)phenyl group, X is a halogen that is fluorine, chlorine, bromine or iodine, and each L is independently a phosphine ligand. Examples of the aryl group Ar^5 are 2,3-bis(trifluoromethyl)phenyl, 2,4-bis(trifluoromethyl)phenyl, 2,5-bis(trifluoromethyl)phenyl, 2,6-bis(trifluoromethyl)phenyl, 3,4-bis(trifluoromethyl)phenyl, and 3,5-bis(trifluoromethyl)phenyl. Of these, 3,5-bis(trifluoromethyl)phenyl is more preferable. The second palladium complex compound may be represented by the following general formula:

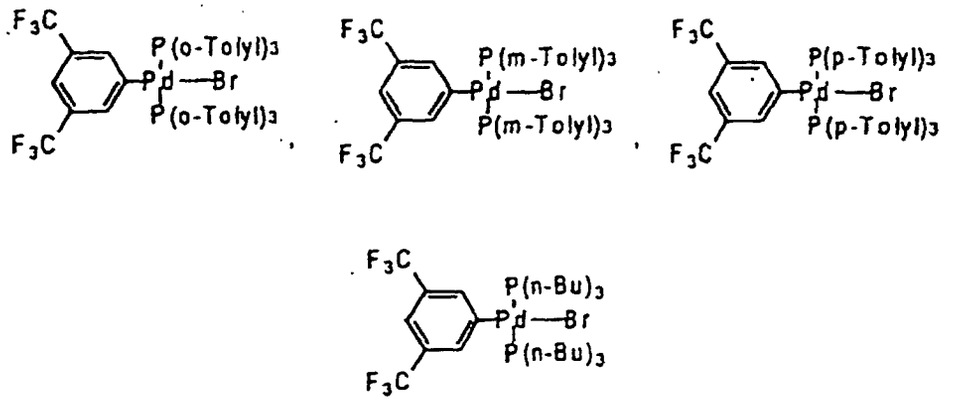


where Ph is phenyl group, and X is a halogen that is fluorine, chlorine, bromine or iodine. Preferable examples of the second palladium complex compound are those represented by the following general formulas:

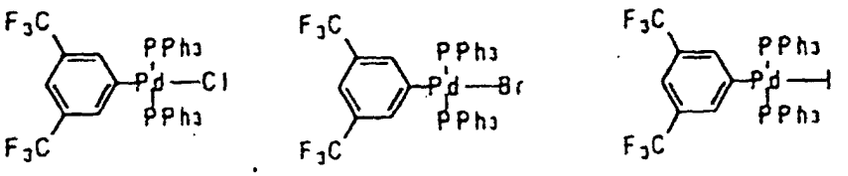






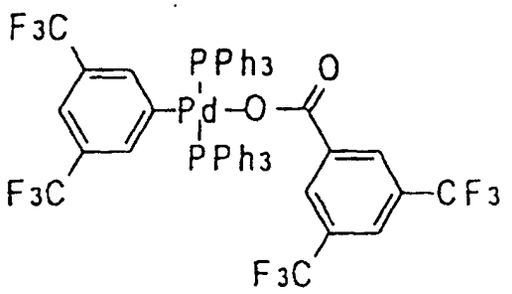


where Ph is phenyl group, Tolyl is tolyl group, and n-Bu is n-butyl group. Of these, more preferable examples are those represented by the following formulas.



The phosphine ligand of the novel first palladium complex compounds is not particularly limited, and is the same as the phosphine used in the first and second methods. Therefore, all the above descriptions of the phosphine used in the first and second methods is applicable to that of the novel first palladium complex compound.

[0033] The novel first palladium complex compound can be crystalline, can be dissolved in various organic solvents, thereby becoming stable. Furthermore, these compounds are each stable in the air at room temperature. Due to such physical and chemical properties of these compounds, it becomes easy to isolate these compounds, thereby making them high in purity. Furthermore, it is easy to store these compounds, thereby making them easy to be handled in an industrial scale use. The novel first palladium complex compounds has catalytic activity in various reactions, such as (1) carbonylation of an aromatic compound through an insertion of monoxide or the like into a halogenated aryl and the subsequent reductive release, (2) vinylation through an insertion of olefin into a halogenated aryl and the subsequent reductive release, and (3) coupling of a halogenated aryl. For example, an example of the novel first palladium complex compound,
[3,5-bis(trifluoromethyl)benzoato) 3, 5'- bis(trifluoromethyl)-phenylbis(triphenylphosphine)palladium(II), represented by the following formula, has catalytic activity in vinylation through an insertion of olefin into a halogenated aryl and the subsequent reductive release.



[0034] The following nonlimitative examples are illustrative of the present invention. The pressure is expressed in gauze pressure, unless otherwise stated.

EXAMPLE 1

Synthesis of Bromo[3,5-bis(trifluoromethyl)phenyl] bis(triphenylphosphine)palladium(II)

[0035] A stainless steel autoclave was charged with 32.5 g of 3,5-bis(trifluoromethyl)bromobenzene, 25.0 g of palladium acetate, 87.3 g of triphenylphosphine, and 75 ml of tetrahydrofuran, followed by stirring. Then, the autoclave was further charged with 38.0 g of 25% aqueous ammonia. Then, the atmosphere of the autoclave was replaced with nitrogen two times. Then, the nitrogen pressure was adjusted to 3 kg/cm^2, and it was started to stir the mixture. With this, the inside temperature of the autoclave has increased. Then, it was started to heat the autoclave by adjusting an oil bath temperature to 105°C. About 1.8 hr later, the inside temperature has reached 97°C , and the oil bath was removed. Then, the autoclave was cooled down in order to stop the reaction. Then, 200 ml of toluene was added to the reaction liquid, followed by stirring for several minutes. The thus treated liquid was subjected to a vacuum filtration. Then, the obtained solid matter was washed with a small amount of n-hexane and then dried, thereby obtaining 72.1 g of pale green crystals. Then, the crystals were subjected to recrystallization using methylene chloride, thereby obtaining 48.7 g of crystals. The crystals were identified as being bromo [3,5-bis(trifluoromethyl)phenyl]bis(triphenylphosphine) palladium(II) by the following properties:

melting point: (decomposition at a temperature of not lower than 192°C);
IR (KBr:cm-1):3052, 1435, 1443, 1166, 1095, 749, 693, and 517;
^{1}H-NMR:(standard substance: TMS, solvent: $CDCl_3$):
δ ppm 6.75(s,1H), 7.09(s,2H), 7.24·7.37(m,18H), and 7.50-7.55(m,12H); and
^{31}P-NMR: (standard substance: 85% H_3PO_4, solvent: $CDCl_3$)
δ ppm 27.33(s).

EXAMPLE 2

Synthesis of Iodo[3,5-bis(trifluoromethyl)phenyl] bis(triphenylphosphine)palladium(II)

[0036] In this example, Example 1 was repeated except in that the autoclave was charged with 4.00 g of 3,5-bis (trifluoromethyl)iodobenzene, 2.64 g of palladium acetate, 9.29 g of triphenylphosphine, 8.91 g of tetrahydrofuran, and 3.45 g of aqueous ammonia and that the reaction was conducted under a condition that the reaction temperature was in a range of 60-80°C and the reaction time was 3 hr. With this, there was obtained 8.81 g of crystals. The crystals were identified as being iodo[3,5-bis(trifluoromethyl) phenyl]bis (triphenylphosphine)palladium(II) by the following properties:

melting point: (decomposition at a temperature of not lower than 170°C)
^{1}H-NMR:(standard substance: TMS, solvent: $CDCl_3$):
δ ppm 6.75(s,1H), 7.07(s,2H), 7.24-7.37(m,18H), and 7.48-7.56(m,12H).

REFERENTIAL EXAMPLE 1

Synthesis of 3,5-bis(trifluoromethyl)benzoic acid

[0037] A stainless steel autoclave was charged with 400 g of 3,5-bis(trifluoromethyl)bromobenzene, 2.40 g of bromo [3,5-bis(trifluoromethyl)phenyl]bis(triphenylphosphine) palladium(II), followed by mixing. Then, the autoclave was further charged with 291.4 g of triethylamine, 0.887 g of triphenylphosphine, and 200 g of water. While the autoclave was closed, it was started to stir the mixture. Then, the atmosphere of the autoclave was replaced with nitrogen three times and then with carbon monoxide three times. The initial pressure of carbon monoxide was adjusted to 3 kg/cm^2, and it was started to heat the autoclave in an oil bath. When the inside temperature reached 104-105°C, the inside pressure was adjusted to 8.5 kg/cm^2. Then, the autoclave was maintained at an inside temperature of 105°C and an inside pressure of 8.5 kg/cm^2, while the amount of carbon monoxide to be introduced was adjusted. About 16 hr later, the heating was stopped, and then the autoclave was cooled down. Then, the inside gas was purged. The reaction liquid was put into a separating funnel, followed by the addition of 200 ml of water. The thus treated liquid was dropped by a dropping funnel to 370 g of a 6N-HCl aqueous solution contained in a 2-liter beaker, while this solution was maintained at a temperature of 20-30°C and stirred. With this, crystals were precipitated, then separated by vacuum filtration, and then washed with 1120 ml of water and then 336 ml of cooled toluene, thereby obtaining 279 g of colorless crystals of 3,5-bis(trifluoromethyl)benzoic acid.

EXAMPLE 3

Synthesis of Trans-[3,5-bis(trifluoromethyl)benzoato]3',5'-bis (trifluoromethyl)phenylbis(triphenylphosphine)palladium (II)

[0038] At first, Example 1 was repeated except that the recrystallization was omitted, thereby obtaining pale green crystals of bromo[3,5-bis(trifluoromethyl)phenyl]bis (triphenylphosphine)palladium (II). Then, a stainless steel autoclave was charged with 70.0 g of the obtained bromo[3,5-bis(trifluoromethyl)phenyl]bis(triphenylphosphine) palladium (II), 39.1 g of 3,5-bis(trifluoromethyl)benzoic acid, and 150 ml of tetrahydrofuran, followed by mixing and stirring. The autoclave was further charged with 20.5 g of 25% aqueous ammonia. Then, the atmosphere of the autoclave was replaced with nitrogen two times. Then, the nitrogen pressure was adjusted to 3 kg/cm^2, and it was started to stir the mixture. Then, it was started to heat the autoclave by adjusting an oil bath temperature to 100°C. About 2 hr later, the oil bath was removed. Then, the autoclave was cooled down. Then, 500 ml of toluene and 200 ml of 25% aqueous ammonia were added to the reaction liquid, followed by stirring for several minutes. Then, an upper organic layer (toluene layer) was washed with water two times and then with a saturated brine, then dried with anhydrous magnesium sulfate, and then concentrated by distilling volatile matters off, thereby obtaining 75.3 g of pale yellow crystals. The crystals were identified as being trans-[3,5-bis(trifluoromethyl)benzoato]3',5'-bis (trifluoromethyl)phenylbis(triphenylphosphine)palladium(II) by the following properties:

melting point: 168-170°C (decomposition);
IR (KBr:cm-1): 3060, 2926, 1637, 1437, 1321, 1277, 1173, 1127, 748, 697, and 518;
^{1}H-NMR:(standard substance: TMS, solvent: $CDCl_3$):
δ ppm 6.97(s,1H), 7.09(s,2H), 7.20-7.32(m,18H), 7.40-7.50(m,12H), 7.53(s,2H), and 7.62(s,1H); and
^{31}P-NMR: (standard substance: 85% H_3PO_4, solvent: $CDCl_3$):
δ ppm 25.73(s).

EXAMPLE 4

Synthesis of [3,5-bis(trifluoromethyl)benzoato]3',5'-bis (trifluoromethyl)phenylbis(triphenylphosphine)palladium(II)

[0039] A stainless steel autoclave was charged with 65.3 g of 3,5-bis(trifluoromethyl)bromobenzene, 100 ml of tetrahydrofuran, 50.0 g of palladium acetate, 175.5 g of triphenylphosphine, 57.6 g of 3,5-bis(trifluoromethyl)benzoic acid, and 60.8 g of 25% aqueous ammonia. Then, the atmosphere of the autoclave was replaced with nitrogen two times. Then, the nitrogen pressure was adjusted to 3 kg/cm^2, and it was started to stir the mixture. With this, the inside temperature of the autoclave has increased to about 50°C. Then, it was started to heat the autoclave by adjusting an oil bath temperature to 120°C. About 2 hr later, the inside temperature has reached 95.6°C, and the oil bath was removed. Then, the autoclave was cooled down. Then, 200 ml of water and 600 ml of toluene were added to the reaction liquid, followed by stirring for several minutes. The thus treated liquid was subjected to a vacuum filtration. An organic layer (upper layer) of the obtained filtrate was washed two times with a saturated brine, then dried with anhydrous magnesium sulfate, and then concentrated by distilling volatile matters off. Solid matter precipitated at the initial stage of this concentration was separated by filtration. Furthermore, the filtrate was concentrated, and then n-hexane was added thereto, followed by cooling. Then, the precipitated solid matter was separated by filtration, thereby obtaining 187.5 g of a crude product. This crude product was subjected to recrystallization using toluene, thereby obtaining 143.0 g of pale yellow crystals. The crystals were identified as being [3,5-bis(trifluoromethyl)benzoato]3',5'-bis(trifluoromethyl) phenylbis(triphenylphosphine)palladium(II) by the following properties:

melting point: 168-170°C (decomposition);
IR (KBr:cm-1): 3060, 2926, 1637, 1437, 1321, 1277, 1173, 1127, 748, 697, and 518;
^{1}H-NMR:(standard substance: TMS, solvent: $CDCl_3$):
δ ppm 6.97(s,1H), 7.09(s,2H), 7.20-7.32(m,18H), 7.40-7.50(m,12H), 7.53(s,2H), and 7.62(s,1H); and
^{31}P-NMR: (standard substance: 85% H_3PO_4, solvent: $CDCl_3$):
δ ppm 25.73(s).

EXAMPLE 5

Synthesis of [3,5-bis(trifluoromethyl)benzoato]3'-trifluoromethylphenylbis(triphenylphosphine)palladium(II)

[0040] A stainless steel autoclave was charged with 25.0 g of 3-trifluoromethylbromobenzene, 75 ml of tetrahydro-

furan, 25 g of palladium acetate, 87.3 g of triphenylphosphine, 38 g of 25% aqueous ammonia, and 57.5 g of 3,5-bis (trifluoromethyl)benzoic acid. Then, the same procedures of Example 4 were repeated, thereby obtaining 32.3 g of a reaction product. This reaction product was identified as being [3,5-bis(trifluoromethyl)benzoato]3'-trifluoromethylphenyl bis(triphenylphosphine)palladium(II) by the following properties:

^{1}H-NMR:(standard substance: TMS, solvent: $CDCl_3$):
δ ppm 6.47(dd, J=7.3, 7.8Hz, 1H), 6.77(d, J=7.3Hz, 1H), 6.80(brs, 1H), 6.95(d, J=7.8Hz, 1H), 7.24-7.30(m, 18H), and 7.40-7.46(m, 12H).

REFERENTIAL EXAMPLE 2

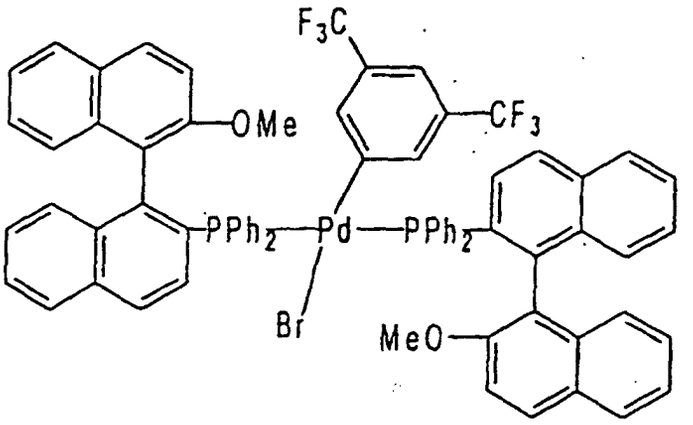
Synthesis of 3,5-bis(trifluoromethyl)cinnamic acid n-butyl ester

[0041] At first, 9.02 g of a vacuum-dried anhydrous sodium acetate was put into a 200 ml flask. Under nitrogen stream, 29.3 g of 3,5-bis(trifluoromethyl)bromobenzene, 15.4 g of n-butyl acrylate, 210 mg of [3,5-bis(trifluoromethyl) benzoato] 3',5'-bis (trifluoromethyl)phenylbis(triphenylphosphine) palladium(II) (the palladium complex compound prepared in Example 4), and 70 ml of N,N-dimethylacetoamide. Then, the flask was heated in an oil bath with stirring. After conducting the reaction for about 1 hr at 110°C, the reaction liquid was cooled down to room temperature. Then, the reaction liquid was poured into an iced water. Organic matter of the reaction liquid was extracted by ether. The obtained organic layer (ether layer) was separated from the aqueous layer, then washed with water three times and then with a saturated brine two times, and then dried with anhydrous magnesium sulfate. Then, the solvent was distilled off under vacuum using an evaporator, thereby obtaining a brown solid matter as residue. This solid matter was subjected to recrystallization using n-hexane, thereby obtaining 22.3 g of crystals. The crystals were identified as being 3,5-bis(trifluoromethyl) cinnamic acid n-butyl ester by the following properties:

melting point: 47-48°C (decomposition); and
^{1}H-NMR:(standard substance: TMS, solvent: $CDCl_3$):
δ ppm 0.975(t, J=7.3Hz, 3H), 1.38-1.50(m, 2H), 1.66-1.75(m, 2H), 4.25(t, J=6.6Hz, 2H), 6.57(d, J=16Hz, 1H), 7.70 (d, J=16Hz, 1H), 7.86(s, 1H), and 7.93(s, 2H).

EXAMPLE 6

[0042] A 100 ml pressure-tight reaction tube replaced with argon was charged with 204 mg (0.91 mmol) of palladium acetate, 1.28 g (2.72 mmol) of (S)-2-methoxy-2'-(diphenylphosphino)-1,1'-binaphthyl[(S)-MeO-MOP], 266 mg (0.91 mmol) of 3,5-bis(trifluoromethyl)bromobenzene, and 1 ml of tetrahydrofuran, followed by mixing and stirring. Then, 0.5 ml of 28% aqueous ammonia was added thereto, and then the atmosphere of the reaction tube was replaced again with argon. After that, the reaction tube was tightly closed without adding pressure thereto. Then, the reaction tube was heated for 6 hr in an oil bath of 110°C, followed by cooling down to room temperature. Then, 1 ml of pure water and 3 ml of toluene were added to the reaction liquid, followed by stirring for several minutes. The thus treated liquid was subjected to a vacuum filtration. The obtained filtrate was washed with a saturated brine two times, then dried with anhydrous magnesium sulfate, and then concentrated, thereby obtaining a mixture in the form of a brown syrup. The obtained mixture was subjected to a thin-layer chromatography using a neutral silica gel column (methylene chloride : hexane = 1:1). With this, a product having a Rf value of 0.50 (hexane : ethyl acetate = 2:1) was obtained with a yield of 22.1%. This product was identified as a palladium complex compound [MBT-Pd-Br((S)-MeO-MOP) having the following formula, by the following properties:

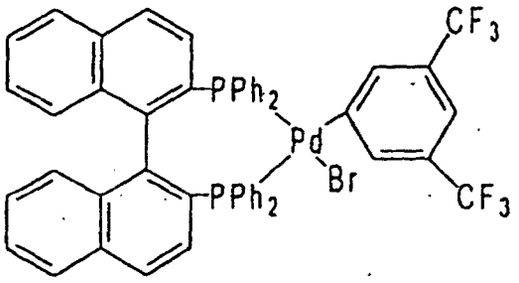


^{1}H-NMR: (300MHz, standard substance: TMS, solvent: $CDCl_3$):
δ ppm: 3.35(s, 6H), 6.48-6.63(m, 9H), 6.65-6.80(m, 10H), 6.85-6.95 (m, 4H), 7.04-7.16(m, 10H), 7.27 (bs, 1H), 7.50-7.60(m, 7H), 7.95(d, 2H, J=8.1Hz), 8.05(d, 2H, J=8.7Hz), and 8.84-8.95 (m, 2H); and
IR (KBr powder: cm^{-1}): 3060, 1626, 1595, 1512, 1435, 1342, 1276, 1253, 1178, 1127, 1087, 878, 806, 745, and 690.

[0043] The procedures for obtaining the above palladium complex compound were repeated except in that (S)-MeO-MOP was replaced with (R)-2-methoxy-2'-(diphenylphosphino)-1,1'-binaphthyl [(R)-MeO-MOP], thereby obtaining another palladium complex compound [MBT-Pd-Br((R)-MeO-MOP)] that is a stereoisomer (R-configuration) of the above palladium complex compound.

EXAMPLE 7

[0044] A 100 ml pressure-tight reaction tube replaced with argon was charged with 449 mg (2 mmol) of palladium acetate, 1.83 g (3 mmol) of (R)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl[(R)-BINAP], 586 mg (3 mmol) of 3,5-bis(trifluoromethyl)bromobenzene, and 2 ml of tetrahydrofuran, followed by mixing and stirring. Then, 1 ml of 28% aqueous ammonia was added thereto, and then the atmosphere of the reaction tube was replaced again with argon. After that, the reaction tube was tightly closed without adding pressure thereto. Then, the reaction tube was heated for 6 hr in an oil bath of 110°C. Then, the reaction tube was cooled down to room temperature. Then, 2 ml of pure water and 6 ml of toluene were added to the reaction liquid, followed by stirring for several minutes. The thus treated liquid was subjected to a vacuum filtration. The obtained filtrate was washed with a saturated brine two times, then dried with anhydrous magnesium sulfate, and then concentrated, thereby obtaining a mixture in the form of a brown syrup. The obtained mixture was subjected to a thin-layer chromatography using a neutral silica gel column (methylene chloride : hexane = 2:1). With this, a product having a Rf value of 0.38 (hexane : ethyl acetate = 2:1) was obtained with a yield of 38.2%. This product was identified as a palladium complex compound [MBT-Pd-Br((R)-BINAP) having the following formula, by the following properties:



^{1}H-NMR: (300MHz, standard substance: TMS, solvent: $CDCl_3$):
δ ppm: 6.58-6.82 (m, 8H), 6.96-7.16(m, 9H), 7.33 (d, 1H, 7.5Hz), 7.38(d; 1H, 6.3Hz), 7.40-7.64(m, 10H), 7.69(dd, 1H, J=9.0, 1.8Hz), and 7.76-7.94(m, 5H);
^{31}P-NMR: (376MHz, solvent: $CDCl_3$):

δ ppm 14.84(d, J=38.1) and 30.51(d, J=40.0);
^{19}F-NMR: (376MHz, standard substance: BTF, solvent: C_6D_3):
δ ppm -62.98(s); and
IR (KBr powder: cm^{-1}): 3060, 1607, 1586, 1572, 1557, 1502, 1483, 1437, 1342, 1311, 1276, 1226, 1176, 1098, 1027, 1000, 880, 837, 816, 743, and 692.

Claims

1. A method for producing a first palladium-complex compound represented by the general formula (4), said method comprising:

(a) reacting an aromatic compound represented by the general formula (1), with a palladium compound and a phosphine derivative, in the presence of a first basic substance, thereby obtaining a second palladium-complex compound represented by the general formula (2); and
(b) reacting said second palladium-complex compound with a benzoic acid represented by the general formula (3), in the presence of a second basic substance, thereby producing said first palladium -complex compound,

$$Ar^1X \quad (1)$$

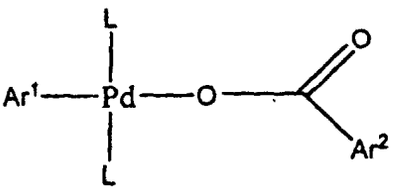
where Ar^1 is an aryl group; and X is a halogen that is fluorine, chlorine, bromine or iodine, trifluoromethanesulfonate group, an alkylsulfonate group having a carbon atom number of 1-4, or a substituted or unsubstituted arylsulfonate group,

$$Ar^1\text{-}PdL_2X \quad (2)$$

where each L is independently a phosphine ligand, and Ar^1 and X are defined as above,

$$Ar^2\text{-}COOH \quad (3)$$

where Ar^2 is an aryl group,



(4)

where Ar^1, Ar^2, and L are defined as above.

2. A method for producing a palladium-complex compound represented by the general formula (4), said method comprising:

reacting an aromatic compound represented by the general formula (1), with a palladium compound, a phosphine derivative and a benzoic acid derivative represented by the general formula (3), in the presence of a basic substance, thereby obtaining said palladium-complex compound,

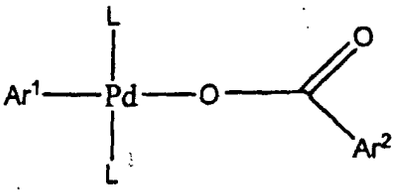
$$Ar^1X \quad (1)$$

where Ar^1 is an aryl group; and X is a halogen that is fluorine, chlorine, bromine or iodine, trifluoromethanesul-

fonate group, an alkylsulfonate group having a carbon atom number of 1-4, or a substituted or unsubstituted arylsulfonate group,

$$Ar^2\text{-}COOH \quad (3)$$

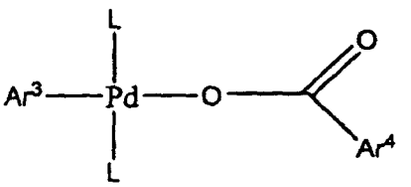
where Ar^2 is an aryl group,



(4)

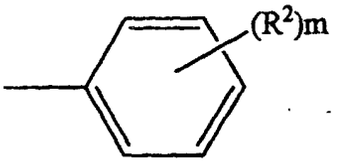
where Ar^1, Ar^2 and X are defined as above, and each L is independently a phosphine ligand.

3. A palladium complex compound represented by the general formula (5),



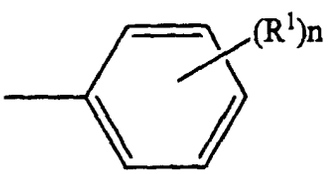
(5)

where Ar^3 and Ar^4 are respectively aryl groups represented by the general formulas (6) and (7), and each L is independently a phosphine ligand,



(6)

where R^2 is trifluoromethyl group, trifluoromethyloxy group, a halogen that is fluorine, chlorine, bromine or iodine, nitro group, acetyl group, cyano group, an alkyl group having a carbon atom number of 1-4, an alkoxyl group having a carbon atom number of 1-4, or an alkoxycarbonyl group having a carbon atom number of 2-5; and m is an integer of 0-4,



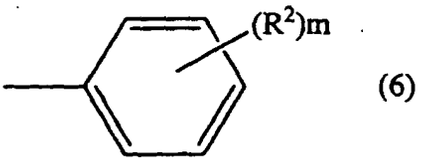
(7)

where R^1 is trifluoromethyl group, and n is an integer of 1-3.

4. A method according to claim 1, wherein said second palladium complex compound is represented by the general formula $Ar^5\text{-}PdL_2X$ where Ar^5 is bis(trifluoromethyl)phenyl group, X is a halogen that is fluorine, chlorine, bromine

or iodine, and each L is independently a phosphine ligand.

5. A method according to claim 1 or 2, wherein said Ar^1 in the general formula (1) is represented by the general formula (6),



(6)

where R^2 is a halogen that is fluorine, chlorine, bromine or iodine, or a monovalent organic group, and m is an integer of 0-4.

6. A method according to claim 5, wherein said monovalent organic group of R^2 in the general formula (6) is trifluoromethyl group, trifluoromethyloxy group, nitro group, acetyl group, cyano group, an alkyl group having a carbon atom number of 1-4, an alkoxyl group having a carbon atom number of 1-4, or an alkoxycarbonyl group having a carbon atom number of 2-5.

7. A method according to claim 1 or 2, wherein said Ar^1 in the general formula (1) is a phenyl group having at least one trifluoromethyl group.

8. A method according claim 1 or 2, wherein said Ar^1 in the general formula (1) is a phenyl group having at least two trifluoromethyl groups.

9. A method according to claim 1 or 2, wherein said aromatic compound is 3,5-bis(trifluoromethyl)bromobenzene or 3,5 - bis(trifluoromethyúiodobenzene.

10. A method according to claim 1 or 2, wherein said X in the general formula (1) is bromine or iodine.

11. A method according to claim 1 or 2, wherein said palladium compound is a palladium salt.

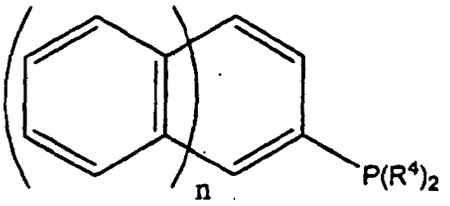
12. A method according to claim 1 or 2, wherein said phosphine derivative is represented by the general formula:

$$P(R^1)_3$$

where each R^1 is independently a first group selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said first group optionally having a first substituent R^2 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a second substituent, said second substituent being selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said second substituent optionally having a third substituent R^3 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a substituent being selected from the group consisting of lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group, said substituent optionally having a substituent.

13. A method according to claim 12, wherein at least one of said R^1 of said phosphine derivative is selected from the group consisting of phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-acynyl group, and 3,5-xylyl group.

14. A method according to claim 12, wherein said phosphine derivative is represented by the following general formula:



where an arbitrary number of hydrogen atoms of naphthalene ring is optionally replaced with said first substituent R^2, and each R4 is independently a group selected from the group consisting of phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-acynyl group, and 3,5-xylyl group.

15. A method according to claim 1 or 2, wherein said phosphine derivative is represented by the general formula $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$ where Q is a bivalent group, and each R^1 is independently a first group selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said first group optionally having a first substituent R^2 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a second substituent, said second substituent being selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said second substituent optionally having a third substituent R^3 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a substituent being selected from the group consisting of lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group, said substituent optionally having a substituent.

16. A method according to claim 15, wherein said bivalent group Q comprises (1) an arbitrary number of a first bivalent group selected from the group consisting of alkylene group, phenylene group, naphthylene group, and anthrylene group, and (2) an arbitrary number of a bonding group selected from the group consisting of single bond, -O-, -S-, -C(=O)-, and -S(=O)-, said first bivalent group optionally having an arbitrary number of a substituent selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group.

17. A method according to claim 15, wherein said bivalent group Q has a substituent optionally and is selected from the group consisting of alkylene group, biphenylene group, binaphthylene group and bianthrylene group, and said substituent of said bivalent group Q is an arbitrary number of a group selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group.

18. A method according to claim 1 or 2, wherein said phosphine derivative is triphenylphosphine.

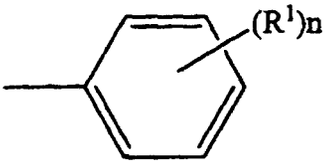
19. A method according to claim 1 or 2, wherein said basic substance is selected from the group consisting of ammonia and amines.

20. A method according to claim 1 or 2, wherein said reacting said aromatic compound is conducted in the presence of a solvent.

21. A method according to claim 1 or 2, wherein said reacting said aromatic compound is conducted in the presence of water as a solvent.

22. A method according to claim 1 or 2, wherein said reacting said aromatic compound is conducted in a single reaction vessel.

23. A method according to claim 1 or 2, wherein said Ar^2 in the general formula (3) is represented by the general formula (7),



(7)

where R^1 is a halogen that is fluorine, chlorine, bromine or iodine, or a monovalent organic group, and n is an integer of 0-3.

24. A method according to claim 23, wherein said monovalent organic group of said R^1 in the general formula (7) is trifluoromethyl group, trifluoromethyloxy group, nitro group, acetyl group, cyano group, an alkyl group having a carbon atom number of 1-4, an alkoxyl group having a carbon atom number of 1-4, or an alkoxycarbonyl group having a carbon atom number of 2-5.

25. A method according to claim 1 or 2, wherein said Ar^2 in the general formula (3) is a phenyl group having at least one trifluoromethyl group.

26. A method according claim 1 or 2, wherein said Ar^2 in the general formula (3) is a phenyl group having at least two trifluoromethyl groups.

27. A method according to claim 1, wherein said reacting said second palladium-complex compound is conducted in the presence of a solvent.

28. A method according to claim 1, wherein said reacting said second palladium-complex compound is conducted in the presence of water as a solvent.

29. A method according to claim 1 or 2, wherein said phosphine ligand is selected from the group consisting of triphenylphosphine, tris(o-tolyl)phosphine, tris(m-tolyl)phosphine, and tris(n-butyl)phosphine.

30. A method according to claim 1, wherein said phosphine ligand in the general formula (2) is triphenylphosphine.

31. A palladium complex compound according to claim 3, wherein said aryl group represented by the general formula (7) is bis(trifluoromethyl)phenyl group.

32. A palladium complex compound according to claim 3, wherein said aryl group represented by the general formula (7) is 3,5-bis(trifluoromethyl)phenyl group.

33. A palladium complex compound according to claim 3, wherein at least one of said R^2 in the general formula (6) is trifluoromethyl group.

34. A palladium complex compound according to claim 3, wherein said aryl group represented by the general formula (6) is phenyl group, trifluoromethylphenyl group or bis(trifluoromethyl)phenyl group.

35. A palladium complex compound according to claim 3, wherein said aryl group represented by the general formula (6) is 3-trifluoromethylphenyl group or 3,5-bis(trifluoromethyl)phenyl group.

36. A palladium complex compound according to claim 3, wherein said aryl group represented by the general formula (6) is phenyl group, 3-trifluoromethylphenyl group or 3,5-bis(trifluoromethyl)phenyl group, and said aryl group represented by the general formula (7) is 3,5-bis(trifluoromethyl)phenyl group.

37. A palladium complex compound according to claim 3, wherein each L in the general formula (5) is represented by the general formula $P(R^3)_3$ where each R^3 is independently (1) a phenyl group optionally having a substituent or (2) an alkyl group having a carbon atom number of 1-6.

38. A palladium complex compound according to claim 37, wherein each R^3 is independently selected from the group

consisting of phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, methyl group, ethyl group and n-butyl group.

39. A palladium complex compound according to claim 3, wherein each L in the general formula (5) is triphenylphosphine.

40. A palladium complex compound according to claim 3, which is [3,5 bis(trifluoromethyl)benzoato]3',5'-bis (trifluoromethyl)phenylbis(triphenylphosphine)palladium(II).

41. A palladium complex compound according to claim 3, which is [3,5-bis(trifluoromethyl)benzoato]3'-trifluoromethylphenylbis(triphenylphosphine)palladium(II).

42. A method according to claim 4, wherein said Ar^5 is 3,5-bis(trifluoromethyl)phenyl group.

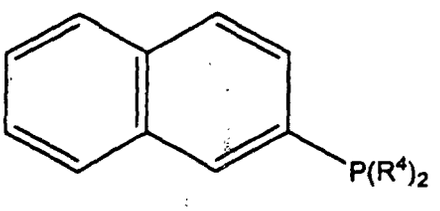
43. A method according to claim 4, wherein each L is represented by the general formula:

$$P(R^1)_3$$

where each R^1 is independently a first group selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said first group optionally having a first substituent R^2 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a second substituent, said second substituent being selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said second substituent optionally having a third substituent R^3 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a substituent being selected from the group consisting of lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group, said substituent optionally having a substituent.

44. A method according to claim 43, wherein at least one of said R^1 of each L is selected from the group consisting of phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-acynyl group, and 3,5-xylyl group.

45. A method according to claim 43, wherein each L is represented by the following general formula:



where an arbitrary number of hydrogen atoms of naphthalene ring is optionally replaced with said first substituent R^2, and each R^4 is independently a group selected from the group consisting of phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-acynyl group, and 3,5-xylyl group.

46. A method according to claim 1 or 2, wherein each L is represented by the general formula $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$ where Q is a bivalent group, and each R^1 is independently a first group selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said first group optionally having a first substituent R^2 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a second substituent, said second substituent being selected from the group consisting of lower alkyl groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group and quinolyl group, said second substituent optionally having a third substituent R^3 selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, and a substituent being selected from the group consisting of lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group, said substituent optionally having a substituent.

47. A method according to claim 46, wherein said bivalent group Q comprises (1) an arbitrary number of a first bivalent group selected from the group consisting of alkylene group, phenylene group, naphthylene group, and anthrylene group, and (2) an arbitrary number of a bonding group selected from the group consisting of single bond, -O-, -S-, -C(=O)-, and -S(=O)-, said first bivalent group optionally having an arbitrary number of a substituent selected from the group consisting of nitro group, primary amino group, secondary amino group, tertiary amino group, halogen atoms, lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group.

48. A method according to claim 46, wherein said bivalent group Q has a substituent optionally and is selected from the group consisting of alkylene group, biphenylene group, binaphthylene group and bianthrylene group, and said substituent of said bivalent group Q is an arbitrary number of a group selected from the group consisting of nitro group, primary amino group, second dary amino group, tertiary amino group, halogen atoms, lower alkyl groups, lower alkoxy groups, cycloalkyl groups, phenyl group, naphthyl group, anthryl group, pyridyl group, and quinolyl group.

49. A method according to claim 4, wherein each L is triphenylphosphine.

Patentansprüche

1. Ein Verfahren zur Herstellung einer ersten Palladiumkomplexverbindung dargestellt durch die allgemeine Formel (4), wobei dieses Verfahren umfasst:

(a) Reagieren einer aromatischen Verbindung dargestellt durch die allgemeine Formel (1) mit einer Palladiumverbindung und einem Phosphinderivat in der Anwesenheit einer ersten basischen Substanz, wobei eine zweite Palladiumkomplexverbindung, dargestellt durch die allgemeine Formel (2) erhalten wird; und

(b) Reagieren dieser zweiten Palladiumkomplexverbindung mit einer Benzoesäure, dargestellt durch die allgemeine Formel (3) in der Anwesenheit einer zweiten basischen Substanz, wobei die erste Palladiumkomplexverbindung

$$Ar^1X \qquad (1)$$

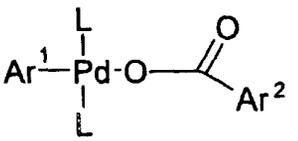
hergestellt wird, in der
Ar^1 eine Arylgruppe; und X ein Halogen, das heisst, Fluor, Chlor, Brom oder Jod, Trifluoromethansulfonatgruppe, eine Alkylsulfonatgruppe mit einer Anzahl Kohlenstoffatome von 1-4 oder eine substituierte oder unsubstituierte Arylsulfonatgruppe ist,

$$Ar1\text{-}PdL_2X \qquad (2)$$

in der jedes L unabhängig voneinander ein Phosphinligand und Ar^1 und X wie oben definiert sind,

$$Ar^2\text{-}COOH \qquad (3)$$

in der Ar^2 eine Arylgruppe ist,



(4)

in der Ar^1, Ar^2 und L wie oben definiert sind.

2. Verfahren zur Herstellung einer Palladiumkomplexverbindung, dargestellt durch die allgemeine Formel (4), wobei dieses Verfahren umfasst:

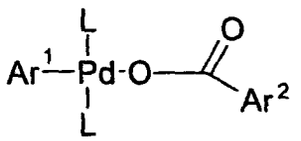
Reagieren einer aromatischen Verbindung, dargestellt durch die allgemeine Formel (1), mit einer Palladiumverbindung, einem Phosphinderivat und einem Benzoesäurederivat, dargestellt durch die allgemeine Formel (3), in der Anwesenheit einer basischen Substanz, wobei die Palladiumkomplexverbindung

$$Ar^1X \quad (1)$$

erhalten wird,
in der Ar^1 eine Arylgruppe und X ein Halogen, das heisst, Fluor, Chlor, Brom oder Jod, eine Trifluormethansulfonatgruppe, eine Alkysulfonatgruppe mit einer Anzahl Kohlenstoffatome von 1-4 oder eine substituierte oder unsubstituierte Arylsulfonatgruppe ist,

$$Ar^2\text{-}COOH \quad (3)$$

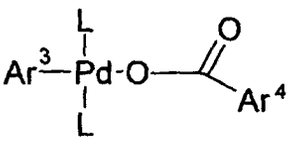
in der Ar^2 eine Arylgruppe ist,



(4)

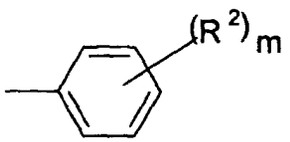
in der Ar^1, Ar^2 und X wie oben definiert sind und jedes L unabhängig voneinander ein Phosphinligand ist.

3. Eine Palladiumkomplexverbindung, dargestellt durch die allgemeine Formel (5)



(5)

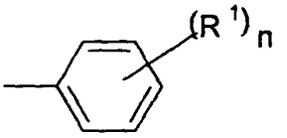
in der Ar^3 beziehungsweise Ar^4 Arylgruppen sind, dargestellt durch die allgemeinen Formeln (6) und (7) und jedes L unabhängig voneinander ein Phosphinligand ist,



(6)

in der R^2 eine Trifluoromethylgruppe, eine Trifluoromethyloxygruppe, ein Halogen, das heisst, Fluor, Chlor, Brom oder Jod, eine Nitrogruppe, Acetylgruppe, Cyanogruppe, eine Alkylgruppe mit einer Anzahl Kohlenstoffatome von 1-4, eine Alkoxygruppe mit einer Anzahl Kohlenstoffatome von 1-4, oder eine Alkoxycarbonylgruppe mit einer

Anzahl Kohlenstoffatome von 2-5 und m eine ganze Zahl von 0-4 ist,

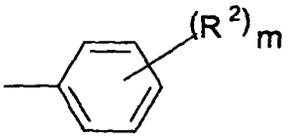


(7)

in der R^1 eine Trifluoromethylgruppe ist und m eine ganze Zahl von 1-3 ist.

4. Ein Verfahren nach Anspruch 1, in dem die zweite Palladiumkomplexverbindung dargestellt ist durch die allgemeine Formel Ar^5-PdL_2X, in der Ar^5 eine bis(Trifluoromethyl)phenylgruppe ist, X ein Halogen, das heisst, ein Fluor, Chlor, Brom oder Jod, ist, und jedes L unabhängig voneinander ein Phosphinligand ist.

5. Ein Verfahren nach Anspruch 1 oder 2, in dem das Ar^1 in der allgemeinen Formel (1) dargestellt ist durch die allgemeine Formel (6)



(6)

in der R^2 ein Halogen, das heisst, Fluor, Chlor, Brom oder Jod oder eine monovalente organische Gruppe ist und m eine ganze Zahl von 0-4 ist.

6. Ein Verfahren nach Anspruch 5, in dem die monovalente organische Gruppe von R^2 in der allgemeinen Formel (6) eine Trifluoromethylgruppe, Trifluoromethyloxygruppe, Nitrogruppe, Acetylgruppe, Cyanogruppe, eine Alkylgruppe mit einer Anzahl Kohlenstoffatome von 1-4, eine Alkoxygruppe mit einer Anzahl Kohlenstoffatome von 1-4 oder eine Alkoxycarbonylgruppe mit einer Anzahl Kohlenstoffatome von 2-5 ist.

7. Ein Verfahren nach Anspruch 1 oder 2, in dem das Ar^1 in der allgemeinen Formel (1) eine Phenylgruppe mit mindestens einer Trifluoromethylgruppe ist.

8. Ein Verfahren nach Anspruch 1 oder 2, in dem das Ar^1 in der allgemeinen Formel (1) eine Phenylgruppe mit mindestens zwei Trifluoromethylgruppen ist.

9. Ein Verfahren nach Anspruch 1 oder 2, in dem die aromatische Verbindung 3,5-bis(Trifluoromethyl)bromobenzol oder 3,5-bis(Trifluoromethyl)iodobenzol ist.

10. Ein Verfahren nach Anspruch 1 oder 2, in dem X in der allgemeinen Formel (1) Brom oder Jod ist.

11. Ein Verfahren nach Anspruch 1 oder 2, in dem die Palladiumverbindung ein Palladiumsalz ist.

12. Ein Verfahren nach Anspruch 1 oder 2, in dem das Phosphinderivat, dargestellt durch die allgemeine Formel:

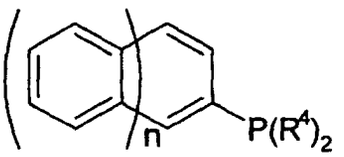
$$P(R^1)_3$$

ist, in der R^1 unabhängig eine erste Gruppe ausgewählt aus der Gruppe bestehend aus niederen Alkylgruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe, wobei die

erste Gruppe wahlweise einen ersten Substituenten R^2, ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen, und einen zweiten Substituenten haben kann, wobei der zweite Substituent ausgewählt ist aus der Gruppe bestehend aus niederen Alkylgruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe, wobei der zweite Substituent wahlweise einen dritten Substituenten R^3, ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen und einen Substituenten ausgewählt aus der Gruppe bestehend aus niederen Alkylgruppen, niederen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe haben kann, wobei der Substituent wahlweise einen Substituenten haben kann.

13. Ein Verfahren nach Anspruch 12, in dem mindestens eines von diesen R^1 des Phosphinderivates ausgewählt ist aus der Gruppe bestehend aus Phenylgruppe, o-Tolylgruppe, m-Tolylgruppe, p-Tolylgruppe, 4-Acynylgruppe und 3,5-Xylylgruppe.

14. Ein Verfahren nach Anspruch 12, in dem das Phosphinderivat dargestellt ist durch die folgende allgemeine Formel:



wobei eine beliebige Anzahl von Wasserstoffatomen des Naphthalinrings wahlweise mit dem ersten Substituenten R^2 ersetzt ist, und jedes R4 unabhängig voneinander ausgewählt ist aus der Gruppe bestehend aus Phenylgruppe, o-Tolylgruppe, m-Tolylgruppe, p-Tolylgruppe, 4-Acynylgruppe und 3,5-Xylylgruppe.

15. Ein Verfahren nach Anspruch 1 oder 2, in dem das Phosphinderivat dargestellt ist durch die allgemeine Formel $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$, in der Q eine bivalente Gruppe ist und jedes R^1 unabhängig voneinander eine erste Gruppe ausgewählt aus der Gruppe bestehend aus niederen Alkylgruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist, die erste Gruppe wahlweise einen ersten Substituenten R^2, ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen, und einen zweiten Substituenten aufweist, wobei dieser zweite Substituent ausgewählt ist aus der Gruppe bestehend aus niederen Alkylgruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe, wobei dieser zweite Substituent wahlweise einen dritten Substituenten R^3 aufweist, ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen und ein Substituent ausgewählt ist aus der Gruppe bestehend aus niederen Alkylgruppen, niederen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe, und Chinolylgruppe und der Substituent wahlweise einen Substituenten aufweist.

16. Ein Verfahren nach Anspruch 15, in dem die bivalente Gruppe Q

(1) eine beliebige Anzahl einer ersten bivalenten Gruppe, ausgewählt aus der Gruppe bestehend aus Alkylengruppe, Phenylengruppe, Naphthylengruppe und Anthrylengruppe und
(2) eine beliebigen Anzahl einer Bindungsgruppe ausgewählt aus der Gruppe bestehend aus einer einfachen Bindung -O-, -S-, -C(=O)- und -S(=O)- ist, wobei die erste bivalente Gruppe wahlweise eine beliebige Anzahl eines Substituenten, ausgewählt aus der Gruppe bestehend aus einer Nitrogruppe, primären Aminogruppe, sekundären Aminogruppe, tertiären Aminogruppe, Halogenatomen, niederen Alkylgruppen, niederen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist.

17. Ein Verfahren nach Anspruch 15, in dem die bivalente Gruppe Q wahlweise einen Substituenten hat und ausgewählt ist aus der Gruppe bestehend aus Alkylengruppe, Biphenylengruppe, Binaphtylengruppe und Bianthrenylgruppe und der Substituent dieser bivalenten Gruppe Q eine beliebige Zahl einer Gruppe, ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Ha-

logenatomen, niederen Alkylgruppen, niederen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist.

18. Ein Verfahren nach Anspruch 1 oder 2, in dem das Phosphinderivat ein Triphenylphosphin ist.

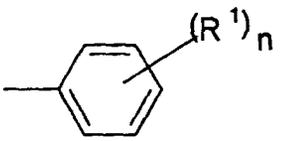
19. Ein Verfahren nach Anspruch 1 oder 2, in dem die basische Substanz ausgewählt ist aus der Gruppe bestehend aus Ammonium und Aminen.

20. Ein Verfahren nach Anspruch 1 oder 2, in dem das Reagieren dieser aromatischen Verbindung in Anwesenheit eines Lösungsmittels durchgeführt wird.

21. Ein Verfahren nach Anspruch 1 oder 2, in dem das Reagieren der aromatischen Verbindung in Anwesenheit von Wasser als Lösungsmittel ausgeführt wird.

22. Ein Verfahren nach Anspruch 1 oder 2, in dem das Reagieren der aromatischen Verbindung in einem einzigen Reaktionsgefäss durchgeführt wird.

23. Ein Verfahren nach Anspruch 1 oder 2, in dem das Ar^2 in der allgemeinen Formel (3) dargestellt ist durch die allgemeine Formel (7),



(7)

in der R^1 ein Halogen, das heisst Fluor, Chlor, Brom oder Iod, oder eine monovalente organische Gruppe und n eine ganze Zahl von 0-3 ist.

24. Ein Verfahren nach Anspruch 23, in dem die monovalente organische Gruppe des R^1 in der allgemeinen Formel (7) eine Trifluoromethylgruppe, eine Trifluoromethyloxygruppe, Nitrogruppe, Acetylgruppe, Cyanogruppe, eine Alkylgruppe mit einer Anzahl Kohlenstoffatome von 1-4, eine Alkoxygruppe mit einer Anzahl Kohlenstoffatome von 1-4, oder eine Alkoxycarbonylgruppe mit einer Anzahl Kohlenstoffatome von 2-5 ist.

25. Ein Verfahren nach Anspruch 1 oder 2, in dem das Ar^2 in der allgemeinen Formel (3) eine Phenylgruppe mit mindestens einer Trifluoromethylgruppe ist.

26. Ein Verfahren nach Anspruch 1 oder 2, in dem das Ar^2 in der allgemeinen Formel (3) eine Phenylgruppe mit mindestens zwei Trifluoromethylgruppen ist.

27. Ein Verfahren nach Anspruch 1, in dem das Reagieren der zweiten Palladiumkomplexverbindung in Anwesenheit eines Lösungsmittels durchgeführt wird.

28. Ein Verfahren nach Anspruch 1, in dem das Reagieren der zweiten Palladiumkomplexverbindung in Anwesenheit von Wasser als Lösungsmittel durchgeführt wird.

29. Ein Verfahren nach Anspruch 1 oder 2, in dem der Phosphinligand ausgewählt ist aus der Gruppe bestehend aus Triphenylphosphin, tris(o-Tolyl)phosphin, tris(m-Tolyl)phosphin und tris(n-Butyl)phosphin.

30. Ein Verfahren nach Anspruch 1, in dem der Phosphinligand in der allgemeinen Formel (2) ein Triphenylphosphin ist.

31. Eine Palladiumkomplexverbindung nach Anspruch 3, in der die Arylgruppe dargestellt durch die allgemeine Formel (7) eine bis(Trifluoromethyl)phenylgruppe ist.

32. Eine Palladiumkomplexverbindung nach Anspruch 3, in der die Arylgruppe dargestellt durch die allgemeinen Formel (7) eine 3,5-bis(Trifluoromethyl)phenylgruppe ist.

33. Eine Palladiumkomplexverbindung nach Anspruch 3, in der mindestens eines der R^2 in der allgemeinen Formel (6) eine Trifluoromethylgruppe ist.

34. Eine Palladiumkomplexverbindung nach Anspruch 3, in der die Arylgruppe dargestellt durch die allgemeine Formel (6) eine Phenylgruppe, Trifluoromethylphenylgruppe oder bis (Trifluoromethyl)phenylgruppe ist.

35. Eine Palladiumkomplexverbindung nach Anspruch 3, in der die Arylgruppe dargestellt durch die allgemeine Formel (6) eine 3-Trifluoromethylphenylgruppe oder 3,5-bis(Trifluoromethyl)phenylgruppe ist.

36. Eine Palladiumkomplexverbindung nach Anspruch 3, in der die Arylgruppe dargestellt durch die allgemeine Formel (6) eine Phenylgruppe, 3-Trifluoromethylphenylgruppe oder 3,5-bis(Trifluoromethyl)phenylgruppe ist und die Arylgruppe dargestellt durch die allgemeine Formel (7) eine 3,5-bis(Trifluoromethyl)phenylgruppe ist.

37. Eine Palladiumkomplexverbindung nach Anspruch 3, in der jedes L in der allgemeinen Formel (5) dargestellt ist durch die allgemeine Formel $P(R^3)_3$, in der jedes R^3 unabhängig voneinander

(1) eine Phenylgruppe, wahlweise mit einem Substituenten oder

(2) eine Alkylgruppe mit einer Anzahl Kohlenstoffatome von 1-6 ist.

38. Eine Palladiumkomplexverbindung nach Anspruch 37, in der jedes R^3 unabhängig voneinander ausgewählt ist aus der Gruppe bestehend aus einer Phenylgruppe, o-Tolylgruppe, m-Tolylgruppe, p-Tolylgruppe, Methylgruppe, Ethylgruppe und n-Butylgruppe.

39. Eine Palladiumkomplexverbindung nach Anspruch 3, in der jedes L in der allgemeinen Formel (5) ein Triphenylphosphin ist.

40. Eine Palladiumkomplexverbindung nach Anspruch 3, die [3,5-bis(Trifluoromethyl)benzoato]3',5'bis (trifluoromethyl)phenylbis(triphenylphosphin)-palladium(II) ist.

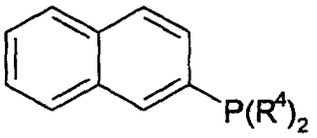
41. Eine Palladiumkomplexverbindung nach Anspruch 3, die [3,5-bis(Trifluoromethyl)benzoato]3'-trifluoromethyl-phenylbis(triphenylphosphin)palladium (II) ist.

42. Ein Verfahren nach Anspruch 4, in dem das Ar^5 eine 3,5-bis(Trifluoromethyl)phenylgruppe ist.

43. Ein Verfahren nach Anspruch 4, in dem jedes L durch die allgemeine Formel $P(R^1)_3$ dargestellt ist, in dem jedes R^1 unabhängig eine erste Gruppe ausgewählt aus der Gruppe bestehend aus niederen Alkygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist, wobei die erste Gruppe wahlweise einen ersten Substituenten R^2 ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen,und einen zweiten Substituenten aufweist, wobei der zweite Substituent ausgewählt aus der Gruppe bestehend aus niederen Alkylgruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist, der zweite Substituent wahlweise einen dritten Substituenten R^3 aufweist, ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen und ein Substituent ausgewählt aus der Gruppe bestehend niederen Alkylgruppen, niederen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist, wobei dieser Substituent wahlweise einen Substituenten aufweist.

44. Ein Verfahren nach Anspruch 43, in dem mindestens eines von diesen R^1 von jedem L ausgewählt ist aus der Gruppe bestehend aus Phenylgruppe, o-Tolylgruppe, m-Tolylgruppe, p-Tolylgruppe, 4-Acynylgruppe und 3,5-Xylylgruppe.

45. Ein Verfahren nach Anspruch 43, in dem jedes L dargestellt ist durch die folgende allgemeine Formel:



in der eine beliebige Anzahl von Wasserstoffatomen des Naphthalinrings wahlweise durch den ersten Substituenten R^2 ersetzt sind und jedes R^4 unabhängig voneinander eine Gruppe ausgewählt aus der Gruppe bestehend aus Phenylgruppe, o-Tolylgruppe, m-Tolylgruppe, p-Tolylgruppe, 4-Acynylgruppe und 3,5-Xynelylgruppe ist.

46. Ein Verfahren nach Anspruch 1 oder 2, in dem jedes L dargestellt ist durch die allgemeine Formel $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$, in der Q eine bivalente Gruppe ist und jedes R^1 unabhängig voneinander eine erste Gruppe, ausgewählt aus der Gruppe bestehend aus niederen Alkylgruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist, wobei die erste Gruppe wahlweise einen ersten Substituenten R^2 ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen, und einen zweiten Substituenten aufweist, wobei der zweite Substituent ausgewählt ist aus der Gruppe bestehend aus niederen Alkylgruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe, wobei der zweite Substituent wahlweise einen dritten Substituenten R^3 aufweist, ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiäter Aminogruppe, Halogenatomen und einem Substituenten, ausgewählt aus der Gruppe bestehend aus niederen Alkylgruppen, trieferen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe, wobei der Substituent wahlweise einen Substituenten aufweist.

47. Ein Verfahren nach Anspruch 46, in dem die bivalente Gruppe Q enthält

(1) eine beliebige Anzahl einer ersten bivalenten Gruppe ausgewählt aus der Gruppe bestehend aus Alkylengruppe, Phenylengruppe, Naphthylengruppe und Anthrylengruppe, und

(2) eine beliebige Anzahl der Bindungsgruppen ausgewählt aus der Gruppe bestehend aus einer Einfachbindung, -O-, -S-, -C(=O)- und -S(=O)-, wobei die erste bivalente Gruppe wahlweise eine beliebige Anzahl eines Substituenten ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen, niederen Alkylgruppen, niederen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe aufweist.

48. Ein Verfahren nach Anspruch 46, in dem die bivalente Gruppe Q wahlweise einen Substituenten aufweist und ausgewählt ist aus der Gruppe bestehend aus Alkylengruppe, Biphenylengruppe, Binaphthylengruppe und Bianthrylengruppe, und der Substituent dieser bivalenten Gruppe Q eine beliebige Anzahl von Gruppen ausgewählt aus der Gruppe bestehend aus Nitrogruppe, primärer Aminogruppe, sekundärer Aminogruppe, tertiärer Aminogruppe, Halogenatomen, niederen Alkylgruppen, niederen Alkoxygruppen, Cycloalkylgruppen, Phenylgruppe, Naphthylgruppe, Anthrylgruppe, Pyridylgruppe und Chinolylgruppe ist.

49. Ein Verfahren nach Anspruch 4, in dem jedes L ein Triphenylphosphin ist.

Revendications

1. Procédé pour la production d'un premier composé complexe de palladium représenté par la formule générale (4), ledit procédé comprenant :

(a) la réaction d'un composé aromatique représenté par la formule générale (1) avec un composé de palladium et un dérivé de phosphine, en présence d'une première substance basique, ce qui permet d'obtenir un second composé complexe de palladium représenté par la formule générale (2) ; et
(b) la réaction dudit second composé complexe de palladium avec un acide benzoïque représenté par la formule générale (3), en présence d'une seconde substance basique, en produisant ainsi ledit premier composé complexe de palladium,

$$Ar^1X \quad (1)$$

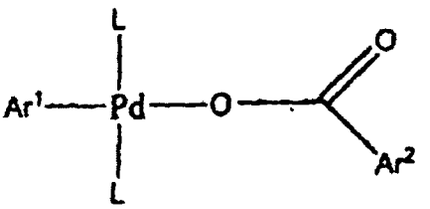
formule dans laquelle Ar^1 représente un groupe aryle ; et X représente un atome d'halogène qui est un atome de fluor, de chlore, de brome ou d'iode, un groupe trifluorométhanesulfonate, un groupe alkylsulfonate ayant 1 à 4 atomes de carbone, ou un groupe arylsulfonate substitué ou non substitué,

$$Ar^{1-}PdL_2X \quad (2)$$

formule dans laquelle chaque groupe L représente indépendamment un ligand phosphine, et Ar^1 et X repondent aux définitions précitées,

$$Ar^{2-}COOH \quad (3)$$

formule dans laquelle Ar^2 représente un groupe aryle,



(4)

formule dans laquelle Ar^1, Ar^2 et L répondent aux définitions précitées.

2. Procédé pour la production d'un composé complexe de palladium représenté par la formule générale (4), ledit procédé comprenant :

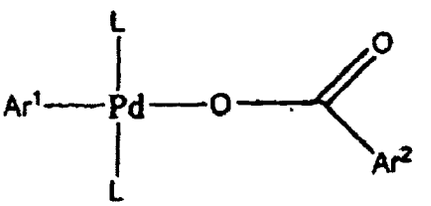
la réaction d'un composé aromatique représenté par la formule générale (1) avec un composé de palladium, un dérivé de phosphine et un dérivé d'acide benzoïque représenté par la formule générale (3), en présence d'une substance basique, ce qui permet d'obtenir ledit composé complexe de palladium,

$$Ar^1X \quad (1)$$

formule dans laquelle Ar^1 représente un groupe aryle ; et X représente un atome d'halogène qui est un atome de fluor, de chlore, de brome ou d'iode, un groupe trifluorométhanesulfonate, un groupe alkylsulfonate ayant 1 à 4 atomes de carbone, ou un groupe arylsulfonate substitué ou non substitué,

$$Ar^{2-}COOH \quad (3)$$

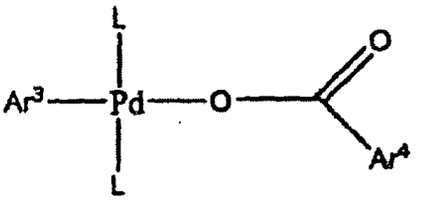
formule dans laquelle Ar^2 représente un groupe aryle,



(4)

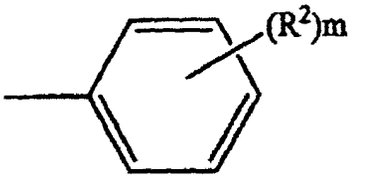
formule dans laquelle Ar^1, Ar^2 et X répondent aux définitions précitées, et chaque groupe L représente indépendamment un ligand phosphine.

3. Composé complexe de palladium représenté par la formule générale (5),



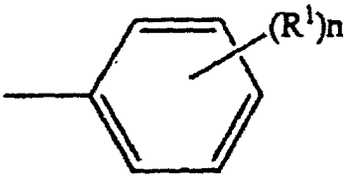
(5)

dans laquelle Ar^1 et Ar^4 sont respectivement des groupes aryle représentés par les formules générales (6) et (7), et chaque groupe L représente indépendamment un ligand phosphine,



(6)

formule dans laquelle R^2 représente un groupe trifluorométhyle, un groupe trifluorométhyloxy, un atome d'halogène qui est un atome de fluor, de chlore, de brome ou d'iode, un groupe nitro, un groupe acétyle, un groupe cyano, un groupe alkyle ayant 1 à 4 atomes de carbone, un groupe alkoxyle ayant 1 à 4 atomes de carbone ou un groupe alkoxycarbonyle ayant 2 à 5 atomes de carbone ; et m représente un nombre entier de 0 à 4,

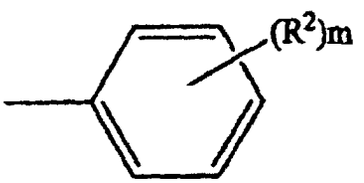


(7)

formule dans laquelle R^1 représente un groupe trifluorométhyle et n représente un nombre entier de 1 à 3.

4. Procédé suivant la revendication 1, dans lequel ledit second composé complexe de palladium est représenté par la formule générale Ar^5-PdL_2X dans laquelle Ar^5 représente un groupe bis(trifluorométhyl)phényle, X représente un atome d'halogène qui est un atome de fluor, de chlore, de brome ou d'iode, et chaque groupe L représente indépendamment un ligand phosphine.

5. Procédé suivant la revendication 1 ou 2, dans lequel ledit groupe Ar^1 dans la formule générale (1) est représenté par la formule générale (6),



(6)

dans laquelle R^2 représente un atome d'halogène qui est un atome de fluor, de chlore, de brome ou d'iode, ou un groupe organique monovalent, et m représente un nombre entier de 0 à 4.

6. Procédé suivant la revendication 5, dans lequel ledit groupe organique monovalent de R^2 dans la formule générale (6) est un groupe trifluorométhyle, un groupe trifluorométhyloxy, un groupe nitro, un groupe acétyle, un groupe cyano, un groupe alkyle ayant 1 à 4 atomes de carbone, un groupe alkoxyle ayant 1 à 4 atomes de carbone ou un groupe alkoxycarbonyle ayant 2 à 5 atomes de carbone.

7. Procédé suivant la revendication 1 ou 2, dans lequel ledit groupe Ar^1 dans la formule générale (1) est un groupe phényle ayant au moins un groupe trifluorométhyle.

8. Procédé suivant la revendication 1 ou 2, dans lequel ledit groupe Ar^1 dans la formule générale (1) est un groupe phényle ayant au moins deux groupes trifluorométhyle.

9. Procédé suivant la revendication 1 ou 2, dans lequel ledit composé aromatique est le 3,5-bis-(trifluorométhyl) bromobenzène ou le 3,5-bis(trifluorométhyl)-iodobenzène.

10. Procédé suivant la revendication 1 ou 2, dans lequel ledit groupe X dans la formule générale (1) représente un atome de brome ou d'iode.

11. Procédé suivant la revendication 1 ou 2, dans lequel ledit composé de palladium est un sel de palladium.

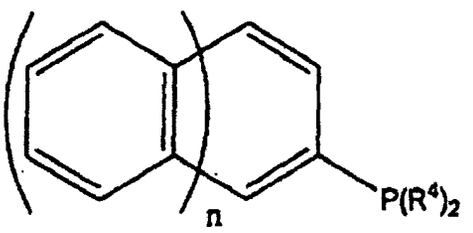
12. Procédé suivant la revendication 1 ou 2, dans lequel ledit dérivé de phosphine est représenté par la formule générale :

$$P(R^1)_3$$

dans laquelle chaque groupe R^1 représente indépendamment un premier groupe choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit premier groupe ayant facultativement un premier substituant R^2 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un second substituant, ledit second substituant étant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit second substituant ayant facultativement un troisième substituant R^3 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un substituant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit substituant ayant facultativement un substituant.

13. Procédé suivant la revendication 12, dans lequel au moins un desdits groupes R^1 dudit dérivé de phosphine est choisi dans le groupe consistant en un groupe phényle, un groupe o-tolyle, un groupe m-tolyle, un groupe p-tolyle, un groupe 4-acynyle et un groupe 3,5-xylyle.

14. Procédé suivant la revendication 12, dans lequel ledit dérivé de phosphine est représenté par la formule générale suivante :



dans laquelle un nombre arbitraire d'atomes d'hydrogène du noyau naphtalène est facultativement remplacé par ledit premier substituant R^2, et chaque groupe R^4 représente indépendamment un groupe consistant en un groupe phényle, un groupe o-tolyle, un groupe m-tolyle, un groupe p-tolyle, un groupe 4-acynyle et un groupe 3,5-xylyle.

15. Procédé suivant la revendication 1 ou 2, dans lequel ledit dérivé de phosphine est représenté par la formule générale $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$ dans laquelle Q représente un groupe bivalent, et chaque groupe R^1 représente indépendamment un premier groupe choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit premier groupe ayant facultativement un premier substituant R^2 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un second substituant, ledit second substituant étant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit second substituant ayant facultativement un troisième substituant R^3 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un substituant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit substituant ayant facultativement un substituant.

16. Procédé suivant la revendication 15, dans lequel ledit groupe bivalent Q comprend (1) un nombre arbitraire d'un premier groupe bivalent choisi dans le groupe consistant en un groupe alkylène, un groupe phénylène, un groupe naphtylène et un groupe anthrylène, et (2) un nombre arbitraire d'un groupe de liaison choisi dans le groupe consistant en une liaison simple, -O-, -S-, -C(=O)- et -S(=O)-, ledit premier groupe bivalent ayant facultativement un nombre arbitraire d'un substituant choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle.

17. Procédé suivant la revendication 15, dans lequel ledit groupe bivalent Q possède facultativement un substituant et est choisi dans le groupe consistant en un groupe alkylène, un groupe biphénylène, un groupe binaphtylène et un groupe bianthrylène, et ledit substituant dudit groupe bivalent Q consiste en un nombre arbitraire d'un groupe choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle.

18. Procédé suivant la revendication 1 ou 2, dans lequel ledit dérivé de phosphine est la triphénylphosphine.

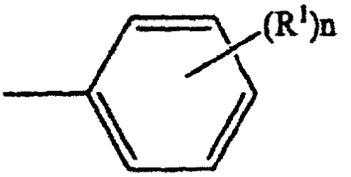
19. Procédé suivant la revendication 1 ou 2, dans lequel ladite substance basique est choisie dans le groupe consistant en l'ammoniac et des amines.

20. Procédé suivant la revendication 1 ou 2, dans lequel ladite réaction dudit composé aromatique est conduite en présence d'un solvant.

21. Procédé suivant la revendication 1 ou 2, dans lequel ladite réaction dudit composé aromatique est conduite en présence d'eau comme solvant.

22. Procédé suivant la revendication 1 ou 2, dans lequel ladite réaction dudit composé aromatique est conduite dans un récipient de réaction unique.

23. Procédé suivant la revendication 1 ou 2, dans lequel ledit groupe Ar^2 dans la formule générale (3) est représenté par la formule générale (7),



(7)

dans laquelle R^1 représente un atome d'halogène qui est un atome de fluor, de chlore, de brome ou d'iode, ou un groupe organique monovalent, et n représente un nombre entier de 0 à 3.

24. Procédé suivant la revendication 23, dans lequel ledit groupe organique monovalent dudit groupe R^1 dans la formule générale (7) est un groupe trifluorométhyle, un groupe trifluorométhyloxy, un groupe nitro, un groupe acétyle, un groupe cyano, un groupe alkyle ayant 1 à 4 atomes de carbone, un groupe alkoxyle ayant 1 à 4 atomes de carbone ou un groupe alkoxycarbonyle ayant 2 à 5 atomes de carbone.

25. Procédé suivant la revendication 1 ou 2, dans lequel ledit groupe Ar^2 dans la formule générale (3) est un groupe phényle ayant au moins un groupe trifluorométhyle.

26. Procédé suivant la revendication 1 ou 2, dans lequel ledit groupe Ar^2 dans la formule générale (3) est un groupe phényle ayant au moins deux groupes trifluorométhyle.

27. Procédé suivant la revendication 1, dans lequel ladite réaction dudit second composé complexe de palladium est conduite en présence d'un solvant.

28. Procédé suivant la revendication 1, dans lequel ladite réaction dudit second composé complexe de palladium est conduite en présence d'eau comme solvant.

29. Procédé suivant la revendication 1 ou 2, dans lequel ledit ligand phosphine est choisi dans le groupe consistant en triphénylphosphine, tris(o-tolyl)phosphine, tris(m-tolyl)phosphine et tris(n-butyl)phosphine.

30. Procédé suivant la revendication 1, dans lequel ledit ligand phosphine dans la formule générale (2) est la triphénylphosphine.

31. Composé complexe de palladium suivant la revendication 3, dans lequel ledit groupe aryle représenté par la formule générale (7) est un groupe bis(trifluorométhyl)phényle.

32. Composé complexe de palladium suivant la revendication 3, dans lequel ledit groupe aryle représenté par la formule générale (7) est un groupe 3,5-bis-(trifluorométhyl)phényle.

33. Composé complexe de palladium suivant la revendication 3, dans lequel au moins un desdits groupes R^2 dans la formule générale (6) est un groupe trifluorométhyle.

34. Composé complexe de palladium suivant la revendication 3, dans lequel ledit groupe aryle représenté par la formule générale (6) est un groupe phényle, un groupe trifluorométhylphényle ou un groupe bis(trifluorométhyl)phényle.

35. Composé complexe de palladium suivant la revendication 3, dans lequel ledit groupe aryle représenté par la formule générale (6) est un groupe 3-trifluorométhylphényle ou un groupe 3,5-bis-(trifluorométhyl)phényle.

36. Composé complexe de palladium suivant la revendication 3, dans lequel ledit groupe aryle représenté par la formule générale (6) est un groupe phényle, un groupe 3-trifluorométhylphényle ou un groupe 3,5-bis-(trifluorométhyl) phényle, et ledit groupe aryle représenté par la formule générale (7) est un groupe 3,5-bis-(trifluorométhyl)phényle.

37. Composé complexe de palladium suivant la revendication 3, dans lequel chaque groupe L dans la formule générale (5) est représenté par la formule générale $P(R^3)_3$ dans laquelle chaque groupe R^3 représente indépendamment (1) un groupe phényle ayant facultativement un substituant ou (2) un groupe alkyle ayant 1 à 6 atomes de carbone.

38. Composé complexe de palladium suivant la revendication 37, dans lequel chaque groupe R^3 est choisi indépendamment dans le groupe consistant en un groupe phényle, un groupe o-tolyle, un groupe m-tolyle, un groupe p-tolyle, un groupe méthyle, un groupe éthyle et un groupe n-butyle.

39. Composé complexe de palladium suivant la revendication 3, dans lequel chaque groupe L dans la formule générale (5) est un groupe triphénylphosphine.

40. Composé complexe de palladium suivant la revendication 3, qui est le [3',5'-bis-(trifluorométhyl)-benzoato] 3', 5'-bis (trifluorométhyl) phénylbis (triphénylphosphine)palladium(II).

41. Composé complexe de palladium suivant la revendication 3, qui est le [3,5-bis-(trifluorométhyl)benzoato]3'-trifluorométhylphényl-bis(triphénylphosphine)palladium(II).

42. Procédé suivant la revendication 4, dans lequel ledit groupe R5 est un groupe 3,5-bis-(trifluorométhyl)phényle.

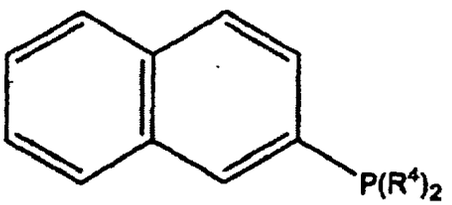
43. Procédé suivant la revendication 4, dans lequel ledit groupe L est représenté par la formule générale :

$$P(R^1)_3$$

dans laquelle chaque groupe R^1 représente indépendamment un premier groupe choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit premier groupe ayant facultativement un premier substituant R^2 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un second substituant, ledit second substituant étant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit second substituant ayant facultativement un troisième substituant R^3 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un substituant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit substituant ayant facultativement un substituant.

44. Procédé suivant la revendication 43, dans lequel au moins un desdits groupes R^1 de chaque groupe L est choisi dans le groupe consistant en un groupe phényle, un groupe o-tolyle, un groupe m-tolyle, un groupe p-tolyle, un groupe 4-acynyle et un groupe 3,5-xylyle.

45. Procédé suivant la revendication 43, dans lequel chaque groupe L est représenté par la formule générale suivante :



dans laquelle un nombre arbitraire d'atomes d'hydrogène du noyau naphtalène est remplacé facultativement par ledit premier substituant R^2, et chaque groupe R^4 représente indépendamment un groupe choisi dans le groupe consistant en un groupe phényle, un groupe o-tolyle, un groupe m-tolyle, un groupe p-tolyle, un groupe 4-acynyle et un groupe 3,5-xylyle.

46. Procédé suivant la revendication 1 ou 2, dans lequel chaque groupe L est représenté par la formule générale $(R^1)_2P\text{-}Q\text{-}P(R^1)_2$ dans laquelle Q représente un groupe bivalent, et chaque groupe R^1 représente indépendamment

un premier groupe choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit premier groupe ayant facultativement un premier substituant R^2 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un second substituant, ledit second substituant étant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit second substituant ayant facultativement un troisième substituant R^3 choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, et un substituant choisi dans le groupe consistant en des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle, ledit substituant ayant facultativement un substituant.

47. Procédé suivant la revendication 46, dans lequel ledit groupe bivalent Q comprend (1) un nombre arbitraire d'un premier groupe bivalent choisi dans le groupe consistant en un groupe alkylène, un groupe phénylène, un groupe naphtylène et un groupe anthrylène, et (2) un nombre arbitraire d'un groupe de liaison choisi dans le groupe consistant en une liaison simple, -O-, -S-, -C(=O)- et -S(=O)-, ledit premier groupe bivalent ayant facultativement un nombre arbitraire d'un substituant choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle.

48. Procédé suivant la revendication 46, dans lequel ledit groupe bivalent Q possède facultativement un substituant et est choisi dans le groupe consistant en un groupe alkylène, un groupe biphénylène, un groupe binaphtylène et un groupe bianthrylène, et ledit substituant dudit groupe bivalent Q est un nombre arbitraire d'un groupe choisi dans le groupe consistant en un groupe nitro, un groupe amino primaire, un groupe amino secondaire, un groupe amino tertiaire, des atomes d'halogènes, des groupes alkyle inférieurs, des groupes alkoxy inférieurs, des groupes cycloalkyle, un groupe phényle, un groupe naphtyle, un groupe anthryle, un groupe pyridyle et un groupe quinolyle.

49. Procédé suivant la revendication 4, dans lequel chaque groupe L représente la triphénylphosphine.